

PRIMARY BATTERIES

Their Theory, Construction and Use

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PREFACE TO THE FIRST EDITION.

PRIMARY BATTERIES form a subject from which much has been hoped, and but little realised, in comparison with the hopes. But even so, it cannot be said that the advance has been small; and consequently no apology is offered for the present volume, in which the somewhat scattered literature of the subject has been brought together.

Recent years have seen important additions to the theory of the voltaic cell, and therefore a considerable number of pages have been devoted to this part of the subject, although it is impossible to do more than give a superficial sketch of the theory in a volume like the present. The reader who is interested in the theory of ionisation should consult such works as those on Electrolysis by Le Blanc and by Lupke, to which the Author desires to acknowledge his indebtedness.

With regard to the practical part of the subject, this volume is not intended to be encyclopædic in character; the object has been rather to describe those batteries which are in general use, or of particular theoretical interest. The Author has also attempted to show what the various kinds of battery, such as Leclanché Cells and Dry Cells, are capable of doing, and to compare the capabilities of one type with another. Very little information is available

on this matter. The Author has therefore included a number of curves which he has obtained experimentally during the last few years, and which enable such comparisons to be made. As far as possible, the Author has drawn on his personal experience, in giving practical results, which, it is hoped, will add to the usefulness of the book.

Owing to the importance of the subject, Standard Cells have been dealt with at some length. Those Cells, however, which are no longer in general use are not described; but recent work is summarised in some detail, so as to give a fair idea of our knowledge up to the present time.

It has also been thought well to devote a Chapter to Carbon Consuming Cells. Very little has been written upon this subject, but it is of great interest, and possibly of great importance in the future.

W. R. COOPER.

LONDON, *Dec*, 1901.

PREFACE TO THE SECOND EDITION.

ALTHOUGH progress in Primary Batteries has not been marked by any startling developments since the date of the first edition of this work, there has nevertheless been steady progress, and consequently many present day batteries are very superior to their predecessors of 15 years ago. For this reason it has been found necessary to rewrite some of the sections and to amplify others to a considerable extent.

A Chapter has been added on Selenium Cells. This seemed desirable, partly because the selenium cell, as distinct from the selenium resistance, is voltaic in its character, but more particularly because selenium has become much more important in recent years, and the literature on the subject is very scattered, receiving but scant attention in ordinary text books.

I desire to thank Mr. F. E. Smith for suggestions and information which have been included in the Chapter on Standard Cells, and to acknowledge the courtesy with which information has been placed at my disposal by many manufacturers.

W. R. COOPER

82, Victoria Street, London, S.W.

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CHAPTER. I.

HISTORICAL.

. At the close of the nineteenth century there was apparently no connection between chemical and electrical energy, the knowledge of electricity being altogether restricted to statical phenomena. Consequently the voltaic cell arose, not as the result of mature reasoning based upon known facts, but rather as the outcome of a chance observation by Galvani. That philosopher observed that recently-skinned frogs, in the neighbourhood of an electrical machine, moved whenever an electrical discharge took place; and, later, that frogs' legs, hung by a copper wire to an iron balcony, were convulsed whenever they touched the iron. From experiments conducted in 1786 it appeared that these movements could be reproduced by connecting the muscles and the nerves by means of a metallic arc, or with an arc partly metallic and partly non-metallic, as, for instance, a metal and a moist piece of wood. To account for these phenomena Galvani* supposed a separation of positive and negative electricity to take place at the junction of nerves and muscles. This view was shown to be erroneous by Volta, who found that such a movement also resulted on connecting two parts of the same muscle by an arc of two metals, such as iron and copper, which thus included a metallic junction. He therefore propounded the idea (known as Volta's Contact Theory), that

* Volta, *Phil. Trans.*, 1793, Part 1. p. 10.

the observed movements are generally due to a force arising from the contact of dissimilar metals, and, in support of this hypothesis, he, constructed in 1799 and described in 1800 a form of dry battery, known as Volta's Pile,* consisting of discs of zinc, wet cloth and copper. These were placed, one above the other, in the order given, so that a piece of wet cloth was always encountered in passing, say, from zinc to copper, but not from copper to zinc on continuing in the same direction. Thus a large number of cells were coupled (as we should now say) in series, and a high E.M.F. resulted, due, according to the theory, to the contacts between the zinc and copper plates.

It is, perhaps, fortunate that wet cloth was used in this pile rather than apparently dry paper, as employed by Zamboni (viz., paper with zinc on one side and manganese peroxide on the other), for it is a comparatively small step to pass from wet cloth to a simple electrolyte, as used by Volta in his "crown of cups."* In this arrangement salt water was contained in a series of cups, the zinc and copper plates of the pile being immersed in the electrolyte, and the zinc in each cup being connected to the copper in the next. Each cup therefore contained the three elements present in the pile, and formed the first example of the simple voltaic element.

In 1801, Davy experimented with acid electrolytes, but they were not readily adopted. The difference between "intensity" and "quantity" was recognised at an early date, and various slight modifications were introduced by Wollaston, Hare and others with the object of reducing the internal resistance.

*Kemp†, followed by Sturgeon‡ in 1830, drew attention to the important diminution of local action brought about by the amalgamation of the zinc plates when used in acid

* *Phil. Trans.*, 1800, Part 2, p. 403.

† *Annals of Electricity*, Vol. I., p. 61, 1836-7.

‡ *Ibid.* Vol. II. p. 68, 1836-7.

editions. The well known cells of Daniell* and of Grove† were described by their inventors in 1836 and 1839 respectively. They mark an epoch, owing to the application of depolarisers in a really practical manner. The true principles underlying polarisation appear to have been realised by Becquerel at an earlier date; in fact, as early as 1829,‡ he described cells of the Daniell type, but these cells were not very practical. By very different reasoning Daniell arrived at the same result, but seems to have realised more fully the conditions necessary for success.

The Smee cell appeared in 1840. In the same year the Grove cell was modified by J. T. Cooper,§ who substituted carbon plates for the platinum foil. This form of cell is, however, generally known by the name of Bunsen,|| to whom we are indebted for the much-used bichromate battery.¶

The Leclanché cell did not appear until 1868, but has been more productive than any other element in the number of modifications that have arisen from it. These include the important class known as "dry cells." A large number of attempts were made in this direction before success was achieved.** Minotto used sand and copper sulphate; Wolf, Keiser, and Schmidt tried sawdust or cellulose; Desruelles filled a Leclanché with asbestos and spun glass, and Pollak made use of a gelatine glycerine. The first really successful dry cell was the Gassner, which appeared in 1888, and since that date the value of this class of cell has steadily improved, so that enormous numbers are manufactured at the present day.

A number of attempts were made from about 1836 to 1888 to obtain electric light commercially from primary batteries. The results, however, were not encouraging, and very little has been done in that direction.

* *Phil. Trans.*, 1836, Part 1, p. 100.

† *Phil. Mag.*, 3rd Series, Vol. XV., p. 287, 1839.

‡ *Annales de Chimie et de Physique*, Vol. XLII., p. 5, 1829.

§ *Phil. Mag.*, 3rd Series, Vol. XVI., p. 35, 1840.

|| *Annalen*, Vol. XXXVIII., p. 311, 1841.

¶ *Pogg. Ann.*, Vol. CXXXL, p. 266, 1843; and Vol. CLV., p. 232, 1875.

** *The Electrician*, Vol. XLII., p. 185, 1839.

In the domain of exact electrical measurement, standard cells play an important part in providing a convenient standard of electrical pressure. At first the Daniell cell was developed for this purpose, particularly by Prof. J. A. Fleming. Later the Clark cell, due initially to the late Latimer Clark, was found to be much superior; but this has now been practically superseded by the Weston or cadmium cell, due to Mr. E. Weston, whose name is so well known in connection with moving coil instruments.

Turning now to the theoretical aspect of the voltaic cell, we find that Volta's Contact Theory was generally accepted on the Continent as the true explanation of Galvani's discovery and the allied phenomena. But there were many, notably in this country, who were disbelievers in the contact theory—among the number Fabroni, one of Volta's countrymen, should not be forgotten. As early as 1800 Nicholson* observed that chemical action took place in both the dry pile and in the "crown of cups." Davy† and Wollaston‡ in 1801 both insisted upon chemical action as being essential to voltaic combinations, and the same line of thought was vigorously upheld by Faraday in his "Experimental Researches" at a later date. In this way there sprang up a school who practically denied the existence of contact force, and who asserted that a current was produced only by chemical action. A dispute, lasting over half a century, arose between the supporters of the Contact Theory on the one hand and those of the Chemical Theory on the other. It was not marked by any decisive victory—a fact which is not surprising, for each side denied, without sufficient ground, a good deal that was claimed by the other, and which has since been shown to be true. But a great deal of valuable scientific work was carried out in support of both of these theories, until, finally, the supporters on either side gradually came to

* *Phil. Mag.*, 1st Series, Vol. VII., p. 337, 1800.

† *Phil. Trans.*, 1801, Part 2, p. 397.

‡ *Ibid.*, 1801, Part 2, p. 427.

admit that truth was also to be found among their adversaries. When the Principle of the Conservation of Energy arose, then mere contact could no longer be regarded as a source of energy. On the other hand, the measurements of Kohlrausch and later investigators established the existence of contact force. The controversy, therefore, died a natural death, only to give place to another, which is still undecided, upon the seat of the electromotive force.

In 1851 Lord Kelvin (then Prof. William Thomson) published his important paper on the dynamical theory of electrolysis, and more recently the voltaic cell has been considered in the light of thermodynamic principles by Helmholtz, Gibbs and others.

In 1887 Arrhenius brought forward his theory of ionisation, which soon found support in the analogy, first pointed out by Van't Hoff in the same year, between osmotic and gaseous pressures; and in 1889 Nernst communicated to the Prussian Academy of Sciences his method of calculating the E.M.F. of various cells. This theory is of very great interest, and has received a deal of attention owing to the important bearing which it has, not only upon voltaic electricity, but also on the theory of solution and other kindred problems.

CHAPTER II.

THE SIMPLE VOLTAIC ELEMENT.

Chemical and Voltaic Action, p. 7.—Definitions, p. 9.—Voltaic Reactions, p. 15.—Electrolysis and the Grotthus Theory, p. 16.—Electro-chemical Series, p. 18.—Electro-chemical Changes in the Simple Voltaic Cell, p. 19.

CHEMICAL AND VOLTAIC ACTION.—When commercial zinc is immersed in dilute sulphuric acid it is dissolved, zinc sulphate is formed, which passes into solution, and hydrogen is rapidly evolved. At the same time energy is liberated and appears in the form of heat. This case of solution may be regarded as an instance of ordinary chemical action.

Electricity in motion being another form of energy, the possibility of transforming the heat of such a chemical reaction into an electrical current at once suggests itself, although the mode of transformation is not obvious. If we replace commercial zinc by the purified metal, we find that very little hydrogen is evolved on dipping it into the sulphuric acid; or, in other words, both the chemical action and the liberation of energy are slight. Now dip a piece of platinum also into the acid, as shown in Fig. 1, without touching the zinc. The reaction is unaffected; but if metallic connection is made between the upper end of the platinum and that of the zinc, the latter is dissolved, and a rapid stream of hydrogen comes from the platinum in addition to that which previously came from

the zinc; and it may be shown that a current of electricity flows at the same time from the platinum through the connection to the zinc. This reaction, however, only takes place when the circuit is closed. The platinum, although apparently attacked, is unaffected; but the zinc is now rapidly dissolved. Yet no heat is evolved in this additional reaction (due to the reaction itself), for this heat is now converted into electrical energy.

We must therefore distinguish between two classes of chemical change.* The first is exemplified by the solution of the zinc when it is not metallically connected with the platinum, in which case the heat evolved cannot be

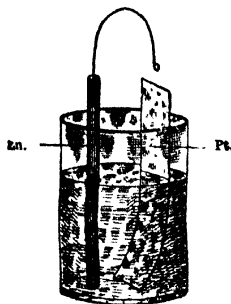


FIG. 1.—Voltaic Solution of Zinc.

utilised electrically. The second case arises when the zinc and platinum are metallically connected. Increased chemical action then takes place; but the increase differs from the original reaction in that the energy liberated is now capable of doing work in an external circuit and is under control. It differs, therefore, in a marked way from ordinary chemical action, and may be termed *electro-chemical* or *voltaic* action.

If perfectly pure zinc could be obtained, it is provable that sulphuric acid alone would be incapable of dissolving

THE SIMPLE VOLTAIC ELEMENT.

if. In such a case, solution would take place only on completing the circuit, as already described, with a plate of platinum, or with some other suitable conductor. The reaction would then be entirely electro-chemical or voltaic in its character. But, since absolutely pure zinc is not obtainable, chemical solution always takes place to some slight extent without closing any external circuit.

This distinction between chemical and voltaic action is convenient, but, in some respects, artificial. In the case of impure zinc, the metal dissolves owing to the presence of impurities which may be looked upon as forming small voltaic couples, as described in Chapter III. Consequently, the reaction, when impure zinc is immersed in sulphuric acid, is really voltaic; but the current flows in what may be termed short-circuited elements, the external circuits of which are through the metal itself, and so cannot be controlled. Therefore the electrical energy is completely transformed into heat. From similar considerations it appears that a great many chemical actions are really voltaic in their origin. The electricity generated is, however, only available under certain conditions, and we shall therefore find it convenient to adhere to the distinction already laid down.

DEFINITIONS.—A **primary battery**, or **cell**, may be defined as a device for the *direct* transformation of chemical energy into electrical energy. Electricity is also obtainable from chemical energy through the medium of *thermopiles*, *steam-driven dynamos*, &c., but the transformation is then an *indirect* one. In a thermopile, chemical combination gives rise to heat, and thence to electrical energy, while a steam-driven dynamo necessitates not only the generation of heat, but also the conversion of this heat into mechanical, and thence into electrical, energy. Since a certain loss of energy always occurs in a transformation of this kind, it follows that

the most direct method of production is generally the most efficient, and therefore a primary battery has the possibility of a higher efficiency than many other generators in common use.

The direction of flow of an electric current is determined in a conventional manner by reference to certain phenomena which are reversed by a change in the direction. We are thus able to say that in a cell, consisting of zinc and platinum in dilute sulphuric acid, the current in the external circuit flows from the platinum to the zinc, but in the cell itself the current flows from the zinc to the platinum. The junctions of the external circuit with the battery plates are generally called the **poles** of the battery; and, as we are most generally concerned with the flow of current in the external circuit, the platinum pole, or upper end of the platinum plate (i.e., the plate by which the current leaves the cell) is called the **positive pole**, and the zinc pole, or upper end of the zinc plate, is called the **negative pole**.

But the zinc plate of a battery is, nevertheless, often spoken of as the **electro-positive plate**, simply because zinc in contact with copper in air becomes positively charged. There are, however, other reasons why the zinc plate should be so designated. As stated above, the current within the cell itself flows from the zinc to the copper; and, moreover, it is the zinc that dissolves. It may, therefore, be looked upon as the chemical source of the current. Consequently, when considering the working of a cell, it is preferable to speak of the zinc as the positive plate; and, in general, it may be said that the positive pole of a cell—viewing it, as it were, from the external circuit—forms part of what is called the negative plate when looking at the cell from the point of view of its internal working. Thus the platinum in a simple element is the positive pole, but the negative plate; similarly, the zinc is the negative pole, but the positive plate. To avoid

Confusion, this distinction must be carefully borne in mind. It is better to use the terms "electro-positive" and "electro-negative" rather than "positive" and "negative", when referring to the plates.

That force which causes the current to flow in any circuit is termed the **electromotive force**, or, more briefly, **E.M.F.** Any cell in a normal condition has a certain E.M.F., more or less definite in its value. This depends mainly on the chemical reaction taking place, and is wholly independent of the dimensions of the cell or size of the plates.

Every cell has a certain resistance, called the **internal resistance**, which impedes the flow of current when the circuit is closed, and which is electrolytic* in its nature. If E is the E.M.F., r the internal resistance, and C the current flowing when the cell is closed through an external circuit of resistance R (containing no E.M.F.), then, since Ohm's law is true for electrolytic resistance, we have the general relation :

$$C = \frac{E}{R + r}.$$

Consequently, the smaller the internal resistance the greater the current for a given external circuit. The magnitude of the internal resistance depends upon the size of the plates, upon their distance apart, and upon the specific resistance of the electrolyte. It is diminished by increasing the area of the plates or by decreasing the distance between them.

A metallic conductor along which a current is flowing is in many ways analogous to a pipe through which water is being forced by a difference of pressure at the two ends. The flow, in the latter case, does not depend upon the *absolute* values of the end pressures, but upon their *difference*. For example, if a reservoir discharges into the

* Any compound body which is decomposed by the passage of an electric current, flowing between electrodes is termed an electrolyte. The internal resistance is electrolytic because every cell contains some electrolyte, such as dilute sulphuric acid.

open air through an orifice 10ft. below the surface of the water, we say that the water is flowing due to a head of 10ft. We are not concerned with the absolute pressures, and consequently we neglect the atmospheric pressure, which is common to both sides of the orifice. So also in a water pipe, the flow depends upon the difference of pressure at the ends.

Similarly, when a current of electricity flows along a wire between any two points, the flow is proportional to what is termed the **difference of potential** between the two points. This statement is embodied in Ohm's law. With the absolute values of the potential itself at the two points we are not concerned, only with the difference. This may be defined as the work done in moving unit quantity of positive electricity from one point to the other in the direction from low to high potential. But such a definition conveys very little idea of the term under consideration, and for practical purposes it seems preferable (though not wholly correct) to look upon potential difference simply as the cause of flow in the conductor.

The reader very naturally enquires: Why introduce the term potential difference when there is already the similar quantity, E.M.F., also causing the current to flow? In reply, it may be said that the E.M.F. of a cell, or of any other source, gives rise to the current and also to the various potential differences in all parts of the circuit, just as the head of water at a waterworks causes the flow of water and differences of pressure in the system of pipes connected with it. In the latter case we should say there exists a difference of pressure in the main between any two points, but we should not say that a certain head of water exists in that part. Similarly, in a metallic conductor at a uniform temperature, forming the external circuit of a cell, it is preferable to say that a potential difference exists between any two points. It may be said that the current flows by reason of the potential difference, or equally that

the potential difference arises by reason of the current flowing. The two statements are merely the result of looking at the same thing from two different points of view. But the E.M.F. does not lend itself to a similar statement, for it is the prime cause of all the phenomena. It is the sum of the potential differences round the circuit. If a wire containing no source of E.M.F. between two points of a circuit were to become a perfect conductor, the potential difference between those points would vanish; but the existence of any E.M.F. in this part of the circuit would not be affected by such a change.

By the correct use of the term potential difference the reader will maintain a mental separation between cause and effect, thereby gaining a clearer conception of the facts, and will at the same time avoid such cumbersome and confusing terms as "terminal E.M.F.," "total E.M.F.," &c., which are sometimes employed.

For a given metallic circuit at a uniform temperature the potential difference between any two points, when a current is flowing, is proportional to the resistance. If V is the potential difference at the terminals, or poles, of a cell when closed through a resistance R , we have a fall of potential V through the external circuit, and therefore, by Ohm's law,

$$V = CR \quad . \quad . \quad . \quad . \quad . \quad (1).$$

But we have also
$$C = \frac{E}{R + r},$$

or
$$RC + rC = E;$$

whence, from (1)
$$V + rC = E,$$

or
$$C = \frac{E - V}{r}.$$

This indicates that, notwithstanding the fact that the internal circuit is complicated by the electromotive force, wherever that may be assumed to exist, yet the current

may be regarded as due to a fall of potential $E - V$ over the internal resistance r . Consequently, we have

$$\frac{E - V}{r} = C = \frac{V}{R},$$

$$\frac{E - V}{V} = \frac{r}{R}, \text{ or } V = \frac{E}{1 + \frac{r}{R}}$$

From this relation we see that when the value of R is infinite—that is, when the cell is on open circuit—the potential difference is equal to the E.M.F. This is also approximately the case when the external resistance is large compared with that of the cell; and, consequently, in practical work, the E.M.F. is often found with sufficient accuracy by means of a high resistance voltmeter, provided the E.M.F. does not suffer any appreciable change due to the small current which, of course, must be generated.

As the value of the external resistance is diminished, the potential difference becomes gradually less in value than the E.M.F., and becomes zero in the extreme case when $R = 0$, or the cell is short circuited. The whole fall of potential then takes place within the cell, and the whole of the energy is dissipated in the form of heat in the internal circuit. There is one case in which the potential difference is always equal to the E.M.F., viz., when $r = 0$, or the internal resistance is zero. Consequently, if it is desirable to have the potential difference constant for different currents, the battery should be made with very small internal resistance. A case of this kind is seen in large secondary cells and supply station batteries.

The letters **P.D.** are sometimes used as an abbreviation for the term potential difference, and, owing to the many analogies with hydraulic distribution, the same quantity is often termed electrical pressure, or pressure simply. Thus

we speak of a current at a pressure of, say, 100 volts, or a current at 100 volts. But the expression "a current of 100 volts" is incorrect, although often used, and is really without meaning. One might as reasonably describe the passage of water through a pipe "as a flow of 100 ft.," or whatever the head might be.

VOLTAIC REACTIONS.—In considering a simple element, such as results by dipping zinc and platinum plates into dilute sulphuric acid, we have seen that the zinc dissolves when a current is produced; but the hydrogen, instead of being given off at the surface of the zinc, is evolved from the platinum. Thus a reaction takes place which is very distinct from ordinary chemical reactions. Changes of a similar kind take place in electrolysis, or when a current is caused to flow through an electrolyte. For example, if two plates or electrodes of platinum dip into dilute hydrochloric acid, and a sufficient potential difference is applied to them, a current flows and the acid is decomposed. But the decomposition does not take place at all points, and the constituents of any molecule do not come off in close proximity. Decomposition only takes place at the two discontinuities where the electrolyte joins the remainder of the circuit. Thus chlorine is evolved at the anode surface, or where the current enters the electrolyte; and hydrogen is evolved at the cathode surface, that is, where the current leaves the electrolyte. Decomposition only takes place at these two surfaces; and, consequently, any theoretical explanation of the phenomena must be based upon some mechanical conception which will sufficiently account for this wide separation of the constituents of a molecule.

Owing to the close connection between voltaic and electrolytic action, we shall do well to briefly consider the explanation of the main facts of electrolysis before discussing further the reactions in a voltaic cell.

CONSIDERATION OF ELECTROLYSIS AND THE THEORY OF GROTTIUS.—In 1805 Grotthus put forward an hypothesis which represents the facts with some accuracy, provided certain assumptions are made with regard to the molecular state of the electrolyte. Unfortunately we know very little about the true nature of a molecule. By the union of equal volumes of hydrogen and chlorine, hydrochloric acid results, and therefore it is convenient to graphically represent a molecule of this acid as $H-Cl$, a bond of union uniting the atom of hydrogen to that of chlorine. But we have no knowledge as to the character of this bond; nor do we know whether the marked want of symmetry here indicated really does exist. But, assuming that molecules differ in some physical property according as they are examined in one direction or another, then we should expect that in a liquid under ordinary conditions there would be no fixed arrangement with regard to this property. For example, suppose that a molecule of hydrogen chloride displays hydrogen to the observer when viewed in a certain direction, and chlorine when the opposite side is seen: then, in a solution of hydrochloric acid, we should generally expect the molecules to be facing in all directions. Some would show hydrogen, some chlorine, and some both hydrogen and chlorine, when viewed from any given point.

When a potential difference is applied to electrodes—for example, platinum plates placed in an electrolyte—Grotthus supposed the molecules to assume a polarised condition, forming chains from one electrode to the other: thus the hydrogen of any molecule in a chain of $H-Cl$ would face the cathode,* and the chlorine the anode. Such an arrangement is indicated in Fig. 2, which represents a section of the electrolyte in a direction perpendicular to the electrode

* The electrode by which the current enters an electrolytic cell is called the *anode*, and that by which it leaves is termed the *cathode*.

plates (which we may suppose placed parallel to each other). If the applied potential difference is sufficient, the attraction of the cathode for the hydrogen and of the anode for the chlorine overcomes the affinity which holds these elements together as a molecule, and decomposition takes place. As the hydrogen goes to the cathode it leaves a chlorine atom in a state of semi-freedom, and the latter, under the influence of the applied potential difference, unites with the hydrogen of the adjacent molecule, giving rise to a second free atom of chlorine in a similar state: this acts upon the next molecule, and so on, until the last chlorine atom at the end of the chain is liberated at the anode. The decomposition may be looked upon as starting simultaneously at both ends of the chain, followed immediately by the intermediate decompositions and recompositions described above.

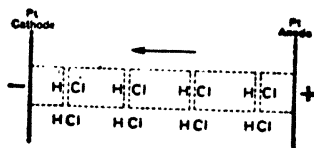


FIG. 2.—The Hypothesis of Grotthius.

Such a theory easily accounts for the evolution of electrolytic products at the electrodes only. It is also in accordance with Faraday's law of definite electro-chemical action; for if we suppose every bond to be capable of carrying a definite quantity of electricity, or being charged with what may be regarded as a unit charge, then the amount of decomposition during any given time will always be directly proportional to the quantity of electricity passing during that time. Further, Faraday's law of electro-chemical equivalence also holds; for a trivalent atom—like aluminium—will have a capacity of three units, a divalent atom—like calcium—will carry

two such quantities, while hydrogen or chlorine, being monovalent, will only carry a single unit. Consequently, the liberation of any atom of a given valency will require the same quantity of electricity as any other of the same valency; but the liberation of a divalent or trivalent atom will respectively require two or three times the quantity necessary for the liberation of a monovalent atom. Thus the number of coulombs sufficient for the liberation of 23 grammes of sodium will liberate only $40/2$, or 20, grammes of calcium, 23 and 40 being the respective atomic weights of these metals; and a given number of coulombs will always liberate the same number of gramme atoms of, say, sodium, potassium, chlorine and bromine, because these elements all have the same valency.

The Grotthus theory, as we shall see later on, does not sufficiently explain all the facts of electrolysis, but it is often an advantage to represent electro-chemical reactions in the light of such an hypothesis, even though it may not be correct, and we shall, therefore, frequently make use of this theory in the consideration of such reactions.

The electrolysis of hydrochloric acid, as above considered, is a very simple case. Electrolytes are frequently far more complicated; but the action of the current, in the first instance at least, invariably consists in splitting the molecules into two parts, which Faraday called the ions. The ion which goes to the anode is known as the anion, and may be termed electro-negative with regard to the electro-positive ion, or cation, which goes to the cathode. These ions may be simple, as in the case of hydrochloric acid, or they may be complex. For example, sulphuric acid, H_2SO_4 , may be split up into the cation H and the anion HSO_4 , or into two monovalent H cations and one divalent anion, viz., SO_4 .

ELECTRO-CHEMICAL SERIES.—It is an important fact that if any two metals are placed in contact, one of them

(which we shall call the first) is found to be positively charged relatively to the second and is said to be electro-positive; equally the second is said to be electro-negative to the first. Similarly, if two such metals are dipped into an electrolyte and their exposed ends are connected metallically so as to form a cell, the electro-positive metal tends to form anions (i.e., to go into solution), cations being deposited on the electro-negative metal. Further, it is found that electro-positive elements tend to form chemical bases, whereas electro-negative elements are relatively acid. In all cases such properties are purely relative, for no element is inherently electro-positive or electro-negative. It is only so in relation to others. As the result of suitable experiments the elements may be arranged in a series such that any one of them is electro-positive compared to all those that follow, while it is electro-negative with regard to those which precede it. In the following series, which is given by Dr. G. Gore, the order must not be looked upon as perfectly invariable: it depends to some extent, at least when considered voltaically, upon the temperature, and upon the nature and concentration of the electrolyte:—

Electro chemical Series.

Caesium	Magnesium	Nickel	Hydrogen	Rhodium	Selenium
Rubidium	Aluminium	Thallium	Mercury	Platinum	Phosphorus
Potassium	Chromium	Indium	Silver	Osmium	Sulphur
Sodium	Manganese	Lead	Antimony	Silicon	Iodine
Lithium	Zinc	Cadmium	Tellurium	Carbon	Bromine
Barium	Gallium	Tin	Palladium	Boron	Chlorine
Strontium	Iron	Bismuth	Gold	Nitrogen	Oxygen
Calcium	Cobalt	Copper	Iridium	Arsenic	Fluorine

ELECTRO-CHEMICAL CHANGES IN THE SIMPLE VOLTAIC CELL.—We are now in a position to consider further the reactions taking place in a simple cell. Voltaic action, or the action occurring in primary batteries, may be looked upon as a case of reversed electrolysis.

By the application of a sufficiently high E.M.F. to two platinum electrodes dipping into dilute hydrochloric acid, decomposition of the acid is effected, hydrogen ions being liberated at the cathode and chlorine ions at the anode. This is indicated in Fig. 3, the E.M.F. being applied by means of a battery, B.

Now replace the anode by a rod of pure zinc, remove the battery, and complete the external circuit by joining the zinc rod with a wire to the platinum cathode. The decomposition again takes place, but the application of an external E.M.F. is no longer necessary. Its place is supplied by the internal E.M.F. of the cell. Hydrogen is

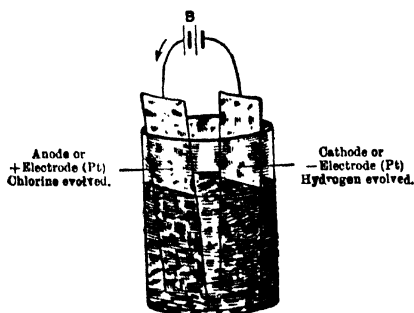


FIG. 3.—Electrolysis of HCl.

still given off at the platinum or negative plate, as indicated in Fig. 4, but chlorine is no longer evolved. The latter combines with the zinc to form zinc chloride, which passes into solution, and we must regard this combination as being very closely connected with the production of the observed E.M.F. This solution of the metal in voltaic action is perfectly definite for a given quantity of electricity, being in accordance with Faraday's laws of electrolysis. The reaction is further indicated diagrammatically in Fig. 5, according to the Grotthius,

theory. As zinc is divalent, two molecules of HCl must be split up to give one molecule of ZnCl_2 . The two H ions

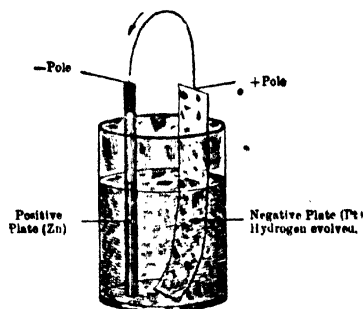


FIG. 4.—Simple Voltaic Cell ($\text{Pt}-\text{HCl}-\text{Zn}$).

liberated at the platinum plate combine to form hydrogen gas, which is evolved.

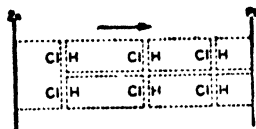


FIG. 5.—Simple Cell with Hydrochloric Acid.

If the electrolyte is dilute sulphuric acid, instead of hydrochloric acid, zinc sulphate results in a precisely

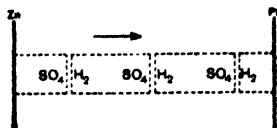


FIG. 6.—Simple Cell with Sulphuric Acid.

similar manner. This is indicated in Fig. 6. But the case of electrolysis of this acid differs from that of

hydrochloric, according to the older theory of electrolysis. The liberated ions in this case are hydrogen and SO_4 . As, however, the latter cannot exist by itself, nor yet by combining with itself, it apparently reacts with the water which is present, re-forming sulphuric acid and liberating oxygen. These changes are represented in Fig. 7, in

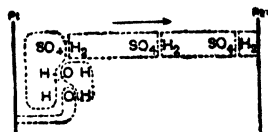


FIG. 7. -Electrolysis of Dilute Sulphuric Acid.

which the SO_4 is regarded as combining with the hydrogen from two molecules of water, leaving two hydroxyl ions free. These two OH ions combine together to form water, and at the same time oxygen is liberated. Thus the result of electrolysis dilute sulphuric acid with electrodes which are not attacked, such as platinum, is the evolution of hydrogen and oxygen. To a superficial observer it would seem that water alone is being decomposed. According to the older view it is preferable to consider that the acid is really the compound which is being decomposed, and that the liberation of oxygen is only due to what is termed a *secondary* electrolytic reaction. Such secondary products and reactions are of frequent occurrence in both electrolytic and voltaic action. On the other hand, according to the more modern theory, it is now commonly held that electrolysis in such cases is simply the electrolysis of water, the effect of the salt or acid being merely to render the water conducting.

*The various forms of simple elements and other cells will be considered later, but it may be remarked in passing that a simple element usually consists of two metallic plates, one of them electro-positive to the other, immersed in a single electrolyte, generally an acid.

CHAPTER III.

LOCAL ACTION. POLARISATION.

Local Action, p. 23.—Amalgamation, p. 24.—Polarisation, p. 26.—Depolarisation, p. 30.—Liquid Depolarisers, p. 32.—Solid Depolarisers, p. 34.—Gaseous Depolarisers, p. 35.—Mechanical Depolarisation, p. 35.—Variation of Internal Resistance, p. 37.

LOCAL ACTION.—We have seen that when a rod of impure zinc is placed in dilute hydrochloric acid it dissolves; and if such zinc is employed as the electro-positive plate in a simple element it dissolves, even when no current is being produced. Consequently, when the cell is in action, the loss of zinc is greater than is demanded by Faraday's law of definite electrolytic decomposition. This solvent action, which supplies no energy to the circuit, is called **Local Action**, and is due to the formation of local voltaic circuits.

The way in which these local circuits are formed will be understood by referring to Fig. 8, which represents a zinc rod immersed in dilute hydrochloric acid, or any other electrolyte.

Suppose the point A to be pure zinc, and B to be an impurity which is electro-negative to zinc, such as lead: then A, B, form a small voltaic cell, having hydrochloric acid as the electrolyte. The external circuit in this case is closed through the zinc rod, and, consequently, a current flows through the electrolyte, from A to B, and the zinc at A is rapidly dissolved.

As already remarked, many cases of chemical action are due to the same cause. In batteries local action

is not restricted to acid electrolytes. It will obviously take place whenever a plate containing electro-negative impurities is brought into a suitable electrolyte, or mixture of electrolytes, such that the combination so formed is capable of acting as a voltaic cell. For example, local action will occur if impure zinc is placed in a hot solution of ammonium chloride, or caustic potash, but the action is far less pronounced in a neutral or alkaline electrolyte than in an acid.

AMALGAMATION.—In 1828 Kemp, followed by Sturgeon, introduced the only effective remedy against local action with which we are acquainted, viz., amalgamation of the

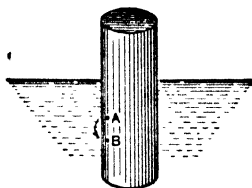


FIG. 8.—Local Action.

zinc. This is readily effected by immersing the zinc in dilute acid and rubbing mercury upon it with a piece of rag. When a bright surface has been obtained, it is found to be no longer attacked, notwithstanding any impurities which may be present.

No complete investigation appears to have been carried out as to why the mercury should afford so complete a protection against the solvent action of the electrolyte. In its voltaic properties the zinc appears to be practically unchanged. For example, the initial E.M.F. of a Clark cell is nearly the same whether the zinc is amalgamated or in its ordinary state. Wright* found that amalgamation lowered the E.M.F. of a Daniell cell by 0.002 volt.

* *Phil. Mag.*, Vol. XIII., p. 265, 1862.

The readiness with which mercury assumes the electro-positive position of zinc through amalgamation is remarkable. Even so small a quantity of this metal as one-millionth has been shown by Hockin and Taylor* to be sufficient to cause this change in the mercury.

By the very nature of local action we should naturally expect such a remedy as that of amalgamation to be ineffective, for the process consists practically in adding an electro-negative impurity to the zinc. The protection afforded by the mercury is often said to be due to a film of hydrogen which is formed by local action, and which adheres to the amalgam, thus preventing the liquid from coming into close contact with the plate. If this were really so it is difficult to see why the electrolyte should be able to come into closer contact when the circuit is closed, and therefore why voltaic action should take place at all; for, although hydrogen is evolved on closed circuit, it is evolved at the negative plate, and cannot be looked upon as *transferred* from the positive. We should also expect the protection to be less effective under reduced pressure.

In order to test the latter point, the author has compared the rates of solution of amalgamated zinc when placed in dilute sulphuric acid—first, under atmospheric pressure, and, secondly, in a vacuum of about 12mm. of mercury. There appeared to be some increased action at the reduced pressure, but the increase was by no means as large as would be expected, supposing the hypothesis to be correct.

As zinc amalgamates very readily, it seems probable that this metal passes at once to the surface of the amalgam, whereas the impurities, being less readily amalgamated, do not pass to the surface. The amalgam would thus act as a filter; but, as soon as it becomes thin, the impurities would project and local action result, which is found to be the case. This way of regarding the matter

* *Jour. Soc. Tel. Eng.*, Vol. VIII, p. 232, 1879.

appears satisfactory enough as far as the impurities are concerned, but it in no way explains the absence of local action between the zinc and the mercury.

It has been suggested by Grove* that the protection is due to polarisation, the hydrogen that is evolved combining with the mercury (or amalgam) and rendering it electro-positive. In support of this idea he states that only a transient current is obtained on opposing *amalgamated* platinum to zinc in dilute acid, and that if this amalgamated plate is then opposed to some unamalgamated platinum a stream of hydrogen is evolved from the latter.

Faraday considered that the mercury produced a uniform condition on the surface, and thus afforded protection.

POLARISATION—When a simple element, consisting, for example, of zinc and platinum in dilute sulphuric acid, is allowed to generate a current, hydrogen is evolved at the platinum plate. At the same time a certain amount of hydrogen adheres to the surface of the platinum and gives rise to an E.M.F. which opposes that of the cell. Consequently, the E.M.F. of the cell diminishes as soon as a current is generated, and the larger the current the more rapid is the fall in E.M.F. This action, due to a product of the electrolysis which is taking place, is known by the name of polarisation.

If the hydrogen were evolved without adhering to the platinum, polarisation in this case would not occur. But a film of hydrogen, coupled with any oxygen in solution at the other plate, forms practically a gas cell, the two gases combining voltaically to form water. Batteries of this class will be considered later in Chapter XII. Now the current, in the external circuit of such a gas cell passes from oxygen to hydrogen, the former being electro-negative to the latter, and, consequently, the E.M.F. is

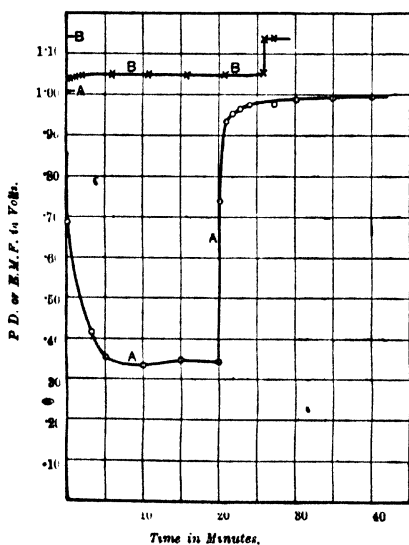
**Phil. Mag.*, 3rd Series, Vol. XV., p. 81. 1839.

opposed to that of the platinum-sulphuric acid-zinc cell. When a simple element is generating a current it may therefore be regarded as a cell consisting of, say, zinc and platinum in sulphuric acid, upon which is superimposed a gas cell with its E.M.F. opposed to that of the cell in question.

Polarisation may be defined as a temporary reduction in E.M.F. due to an alteration of the electrolyte, or of the plates, brought about by the voltaic action of the cell. If this altered condition is removed by suitable means, as quickly as it is produced, the polarisation will no longer exist, and the lowering of E.M.F. due to this cause will be very slight or transient. On the other hand, the E.M.F. becomes permanently lowered as the current is generated, on account of what is generally termed the exhaustion of the cell. For example, the acid in the simple element here considered may become practically neutralised by dissolving the zinc; or the zinc sulphate formed round the zinc plate may diffuse until it reaches the platinum, and zinc is electrolytically deposited upon the surface of the latter: this deposition of zinc causes the platinum to gradually assume the character of a zinc plate, and, therefore, brings about a corresponding fall in the E.M.F. Changes of this kind can only be remedied by setting up the cell afresh, whereas a change due to polarisation passes off more or less rapidly upon allowing the cell to rest.

In Fig. 9 a curve is reproduced which illustrates the rapid polarisation of a simple element. The cell used had an E.M.F. of 1.005 volts, and consisted of copper and zinc in dilute sulphuric acid. It must be remembered that, upon closing the circuit of any cell through a given resistance, the potential difference assumes some value below that of the E.M.F., this initial value depending, *inter alia*, upon the internal resistance of the cell. If no polarisation were to take place, and no change in the internal resistance, the potential difference would remain constant

The internal resistance in the present experiment may be regarded as practically constant. On referring to curve A it is seen that the potential difference fell very rapidly when the cell was closed through a resistance (of 10 ohms), indicating therefore a large amount of polarisation in the case of a simple element. The initial value was probably about 0.85 volt, but it fell to 0.54 in one minute and to 0.355 volt at the end of five minutes. The potential



•FIG. 9.—Polarisation of a Simple Element (A) and of a Daniell Cell (B).

difference then remained fairly constant. At the end of twenty minutes the circuit was broken. It was not possible to observe the value of the E.M.F. immediately on breaking circuit owing to its rapid variation, but after fifteen seconds it is seen to be 0.74 volt, and after one minute it had risen to 0.94 volt. This rise is due to the

diffusion of the hydrogen from the surface of the copper plate. As the quantity of hydrogen diminishes, the rate of diffusion falls off, and, therefore, the rise of E.M.F. becomes slower, as shown by the curve. At the end of twenty minutes the E.M.F. had nearly regained its original value. The same result may be obtained more rapidly by taking the copper plate out of the electrolyte and wiping it so as to remove adhering gas.

The above is the generally accepted explanation of polarisation. W. A. Anthony,* however, prefers the view that polarisation is due to exhaustion of oxygen in the electrolyte immediately in contact with the negative plate. In support of this statement, Anthony finds that if a copper-sulphuric acid-zinc cell is closed through a resistance of three ohms for fourteen hours the E.M.F. falls to 0.53 volt, and does not recover on standing, or on agitating, or on passing nitrogen through the cell. The passage of oxygen, on the other hand, produces a rapid recovery. If the time of closed circuit is short, agitation reduces polarisation, because it brings fresh portions of the electrolyte, which still contain oxygen, into contact with the negative plate.

These experiments do not appear to be quite conclusive. A film of hydrogen is not easily removed by agitation, &c., and dissolved oxygen would no doubt assist recovery. But it does not follow that polarisation is not due to the hydrogen. If this were true, physical depolarisation (which is described later) would be impossible.

Polarisation also occurs at the zinc plate; but it is not so marked as that which arises at the negative plate, and it differs from the latter inasmuch as it is not due to the liberation of an ion, such as hydrogen. This polarisation can be demonstrated by immersing in the cell a copper electrode which is not employed for the purpose of

* *Proc. Amer. Association for Advancement of Science*, Vol. XLVII., pp. 138-140, 1898.

generating a current, and measuring the E.M.F. between this electrode and the zinc and copper respectively of the cell, before and after the external circuit has been closed. The E.M.F. in each case is found to vary. By using a carbon electrode in this manner, B. E. Moore and H. V. Carpenter* have shown that the polarisation in a zinc-ammonium-chloride-carbon cell, working under the conditions of their experiment, takes place mostly at the carbon, and that the recovery on open circuit, or depolarisation, at first takes place chiefly around the zinc.

This method, however, is not wholly free from objection. A part of the E.M.F. observed between the electrode and the zinc plate is due to a difference in concentration caused by the voltaically-formed salt passing into solution. This salt solution is more dilute about the exploring electrode than in the neighbourhood of the zinc plate, and thus forms what is known as a concentration cell. When the difference in concentration vanishes, the part of the E.M.F. due to it will not be observed. Similarly, the E.M.F. between the electrode and the carbon is influenced not merely by the presence of hydrogen upon the carbon, but also by any difference in density. As the concentration E.M.F. between the zinc and carbon diminishes owing to diffusion of the salt, that between the carbon electrode and the carbon plate may increase from the same cause. Consequently, the observed polarisation effects depend, to some extent, upon the position of the exploring electrode.

DEPOLARISATION.—In practice, only polarisation at the electro-negative plate is important, and the polarising ion is generally hydrogen. The earliest attempt at overcoming polarisation in the voltaic cell was made by Becquerel, and, later, by Daniell, who described his well-known battery in 1836. His method consists in separating the zinc and copper of a simple element by a porous pot containing a saturated

* *Phys. Rev.*, Vol. IV., pp. 329-336, 1897.

solution of copper sulphate (*see*, further, Chapter IX., p. 235). The zinc is thus immersed in dilute sulphuric acid, while the copper is surrounded by copper sulphate. The chemical changes which take place on closing the circuit may be represented in the form of a Grotthus chain, as seen in Fig. 10, which should be compared with the corresponding diagram referring to a simple element.

The hydrogen set free by the decomposition of the sulphuric acid is seen to re-form a molecule of acid by interaction with a molecule of copper sulphate, and a copper ion is at the same time set free. Consequently, instead of hydrogen being liberated upon the copper plate, copper only is deposited, and therefore, assuming that the character of this deposit does not differ from that of

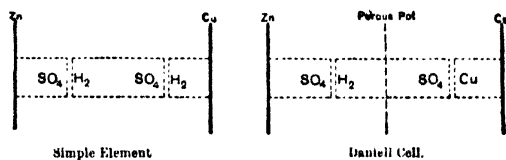


FIG. 10.

the plate, no variation of E.M.F. can occur at this plate (neglecting changes due to variation of concentration). So long as the sulphuric acid can be maintained separate from the copper sulphate, the exchange of copper for hydrogen takes place at their surface of separation. But, since diffusion takes place, the acid, and also the zinc sulphate that is formed, in time reach the copper plate: hydrogen is then evolved, giving rise to polarisation, and zinc may also be deposited. The copper sulphate meanwhile diffuses in the opposite direction and deposits copper upon the zinc as soon as it comes in contact with the zinc plate. Therefore the porosity of the pot, although a necessity, is a defect. We need scarcely remark that the conduction within the cell must be entirely electrolytic, and

thus a permanent separation of the solutions by a metal division is out of the question. If a division of copper, for example, were employed, the cell would be equivalent to a simple element in series with a copper voltameter: hydrogen would be evolved at the surface of the division facing the zinc, and polarisation would in no way be remedied.

In Fig. 9 is given a curve B, obtained by closing the circuit of a Daniell cell through 10 ohms. The same resistance was employed in the case of the simple element as already described. The same plates were used in both cells, but as the E.M.F. of a simple element is lower than that of a Daniell cell, the test was really more severe on the latter. The improvement due to the action of the copper sulphate is very noticeable. In fact, the potential difference is practically constant, and, upon breaking the circuit, the E.M.F. rose very rapidly—as shown by the curve—to its initial value (1.14 volts).

Chemical depolarisers may be divided into three classes: (1) Liquid, (2) solid, and (3) gaseous, and to these must be added a fourth class, which depends upon physical or mechanical means.

LIQUID DEPOLARISERS.—We have already considered an instance of depolarisation by means of a liquid in the case of the Daniell cell. Certain other cells depend upon the same principle, viz., the use of two fluids separated from each other by a porous partition, one of the fluids being the depolariser which surrounds the negative plate, the other acting as a solvent for the positive. Such cells are often termed two-fluid batteries.

The copper sulphate in a Daniell cell may be said to act by substitution, the liberated hydrogen taking the place of the copper as it moves along the Grove chain, and the copper being deposited upon a copper plate. Consequently, the depolarisation, as far as the hydrogen is concerned,

must, under all conditions, be practically perfect, provided the acid does not diffuse to the negative plate.

Instead, however, of substitution, the hydrogen may be first deposited, and then removed by oxidation. The Grove cell, for example, consists of zinc in dilute sulphuric acid, separated by a porous pot from platinum immersed in concentrated nitric acid (see p. 246). The reaction which takes place may be represented diagrammatically as shown in the following figure:—

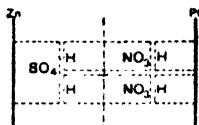
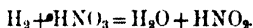


FIG. 11.—Reaction in a Grove Cell.

Here the hydrogen is not replaced by another ion incapable of polarisation. It is, in fact, deposited upon the platinum; but, as soon as the deposition takes place, the hydrogen is oxidised to water by the nitric acid, the reaction in its simplest form being represented according to the equation



The hydrogen is thus removed by the formation of nitrous acid, and polarisation is prevented. In the case of copper sulphate, the depolarising power depends upon the conduction by the salt solution; copper sulphate having no power of oxidation in itself. But depolarisation by nitric acid depends upon the oxidising power of the acid close to the negative plate, and on that account the acid must be concentrated.

The porous pot in a Grove cell cannot be omitted, partly because concentrated acid is necessary, and partly owing to the fact that local action takes place readily if zinc, even when amalgamated, is placed in strong nitric

acid, or in sulphuric acid containing nitric. In some cases, however, the depolariser and the solvent may be mixed together. For example, in the bichromate cell the electrolyte, consisting of sulphuric acid with bichromate of sodium or potassium in solution, is often used without a porous pot. The bichromate alone is not an oxidising agent, and therefore it is necessary that acid should also be present at the negative plate. Around the positive plate, however, the bichromate is unnecessary.

SOLID DEPOLARISERS.—By employing a solid depolariser the use of a porous pot may be avoided, but the depolarisation is not usually so complete as in the case of liquids. Metallic oxides, capable of easy reduction, are used for this purpose in alkaline or neutral solutions. Such oxides would be very effective if they could be placed, as it were, in series with the negative plate (in a manner analogous to the copper sulphate in a Daniell cell), or if they could be made to take the place of the negative plate. In such a case the hydrogen would of necessity be deposited upon an oxidising body, and very little polarisation would then occur. But, owing to the fact that metallic oxides are bad conductors, they cannot well be employed in this simple manner. Manganese peroxide, for example, which is largely used as a depolariser in Leclanché cells (*see* p. 193), is always mixed with carbon, and the mixture either placed round the negative carbon plate or suitably made up for use directly as a plate. Consequently, hydrogen is not necessarily deposited upon the manganese peroxide. It may happen to be deposited upon some of the carbon that is mixed with it, in which case it will not be so readily oxidised. As the action of the cell continues and the peroxide becomes reduced, a larger proportion of hydrogen is deposited upon the carbon, or upon reduced oxide, and consequently the depolarisation becomes less and less effective.

In the Edison-Lalande cell (see p. 176), cupric oxide is employed as a depolariser. The oxide is compressed into a plate which, after the surface has been slightly reduced so as to render it a conductor, is used as the electro-negative plate. The depolarisation is very efficient, although such a result would scarcely be anticipated. As the reduction proceeds into the body of the plate we should expect the hydrogen to be deposited mostly upon the outer surface, and that its ready oxidation would be impeded. The depolarisation is, in fact, found to be less complete as the oxide becomes further removed from the surface.

GASEOUS DEPOLARISERS.—Depolarisation by means of the oxygen in the atmosphere has been attempted, but without much success. In 1878 a cell was described in which the zinc was immersed in dilute sulphuric acid held in a porous pot. Around the latter was coiled a silver wire which played the part of a negative plate. The hydrogen deposited is oxidised by atmospheric oxygen, which is probably taken into solution somewhat readily by the film of acid on the outside of the pot. The cell, it is said, was found to be more constant than a Leclanché, but there are obvious disadvantages in such a form, except for very special applications.

Atmospheric oxygen is also considered to be the depolariser in the Walker-Wilkins cell.

Such a method of depolarisation has, of course, the advantage that the substance employed is inexhaustible and requires no replacement, but it does not appear to be very practicable.

PHYSICAL AND MECHANICAL DEPOLARISATION.—Although a film of gas adheres more or less tenaciously to a smooth plate immersed in a liquid, it is evolved with comparative ease from a roughened surface. Depolarisa-

tion may, therefore, be effected without any chemical reaction involving the use of an oxidising or other agent, by suitably preparing the surface of the negative plate. In the Smee cell (*see* p. 149), which depends upon this principle, the negative consists of a silver or platinum plate, upon which platinum has been electrolytically deposited. A roughened surface is thus obtained from which the hydrogen is far more readily evolved than it would be from a silver or platinum plate in the ordinary condition. The electrolyte of the Smee cell is sulphuric acid, the positive plate being zinc.

Considering the simplicity and general convenience of physical depolarisation, it is surprising that more attention has not been given to the subject. The method has been revived in the Velvo Carbon cell (*see* p. 150), apparently its only application to a cell consisting of inexpensive materials.

In what precedes we have looked upon hydrogen as being the only polarising ion in voltaic action. That, however, is not the case. For example, zinc sulphate may be used in a Daniell cell in place of sulphuric acid; and the polarising ion is then zinc instead of hydrogen. In the Clark cell (*see* p. 238), the electrolyte is practically a saturated solution of zinc sulphate, and polarisation is again due to zinc. If the electrolyte is caustic soda, as in the Edison-Lalande cell, then sodium is the polarising ion. By reacting with the water of the solution, this gives rise to hydrogen as the final liberated ion at the negative, but polarisation, in the first instance, is really due to sodium.

In addition to physical depolarisation, purely mechanical means have sometimes been employed, the plates being given a motion so as to bring parts alternately under polarising and depolarising influences. Also motion of the electrolyte has been used to maintain its depolarising qualities constant, as in the Benkō cell.

The influence of depolarisers upon the E.M.F. of a cell will be considered in the next chapter.

VARIATION OF INTERNAL RESISTANCE.—When a cell is freshly set up and has not been used, it may be considered to have a certain definite internal resistance, depending chiefly upon the specific resistance of the electrolyte, upon the size of the plates and their distance apart. But when a current is generated, various compounds are electrolytically formed, and, therefore, the value of the internal resistance changes. It is also observed to vary according to the strength of current flowing. In the case of the early Gassner dry cell,

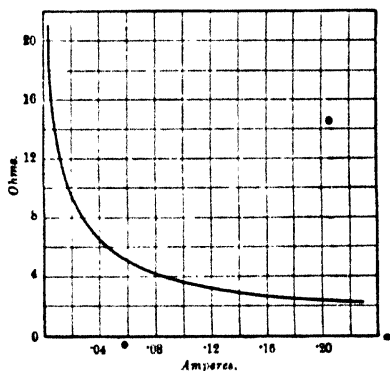


FIG. 12.—Variation of Internal Resistance with the Current Generated.

Carhart* found this effect to be very marked. The results obtained are reproduced in Fig. 12 in the form of a curve. With a current of 2.8 milliamperes the resistance amounted to 21.1 ohms, whereas it fell to 2.29 ohms when the current rose to 228.9 milliamperes. From the above it appears that the internal resistance of a cell is a somewhat indefinite quantity, varying not only with the electrolytic changes taking place, but also with the strength of current

* *Phys. Rev.*, Vol. II., p. 392, 1894-5; or *The Electrician*, Vol. XXV p. 18, 1895.

generated. This variation of internal resistance may, however, be more apparent than real. Assuming Wiedeburg's theory of polarisation, Mr. K. E. Guthe* has shown that the true value of the resistance is constant, although the apparent resistance varies, according to the theory, in a manner closely resembling the preceding curve.

Wiedeburg's theory is based upon the idea that polarisation is due to the collection of ions on the electrodes, which causes a change in density in the neighbouring solution and thus produces a counter E.M.F. Only a certain proportion of the ions are supposed to be active.

When a battery is closed through an external resistance which is maintained constant, the current will generally be found to vary very soon. It may fall owing to polarisation, or, later, owing to exhaustion of the cell. Increase in the internal resistance will have the same effect; but, if a decrease takes place, it may, under some conditions, be more than sufficient to compensate for the polarisation, and in such a case the current will be found to increase to some extent as time goes on; although finally a decrease must, of course, take place. An example of this effect is shown in curve B of Fig. 9, and also in Fig. 55.

* *Phys. Rev.*, Vol VII., pp. 193-198, 1898.

CHAPTER IV.,

*THEORY OF THE VOLTAIC CELL.

Constitution of the Voltaic Cell, p. 39.—Thermal Relations, p. 42.—The Helmholtz Equation and its Application, p. 45.—Exceptions to the Helmholtz Equation, p. 52.—Temperature Co-efficient as a Thermo-Electric Effect, p. 53.—Chemical and Contact Theories, p. 55.—Contact Force, p. 57.—Seat of the E.M.F., p. 56.—Conclusions, p. 82.

CONSTITUTION OF THE VOLTAIC CELL.—So far we have chiefly considered the very simplest form of cell. But the broad question naturally arises: What are the essential conditions that must be fulfilled by the constituents in order that a voltaic cell should result? They appear to be the following:—

1. At least three elements are necessary.
2. One of these must be a conductor of the first class (*i.e.*, not decomposed by the passage of a current); one must be of the second class (*i.e.*, an electrolyte); the third may belong to either of these two classes.
3. It is necessary that two of these constituents should be capable of chemical interaction. It is not, however, necessary that the reaction should take place upon the mere contact of the substances under ordinary conditions. Such a reaction may be impossible in the ordinary way, although taking place readily in a voltaic circuit.
4. Finally, the liberation of an ion is necessary. The ion so liberated may give rise to the corresponding

molecule as one of the final products; or it may in some way enter into combination with some other body. Consequently, although an ion is liberated, it is not necessarily evolved in the corresponding molecular state. This condition merely implies that the primary decomposition of the electrolyte must be voltaic, not simply chemical. Perhaps a more general statement would be that, in their voltaic action, a separation of the electro-positive from the electro-negative ions must take place.

Some apparent exceptions to these four conditions will be considered in Chapter VI.

Most cells consist of two different conductors of the first class combined with one or more electrolytes. It is, however, possible to reverse the arrangement and to combine two electrolytes with one conductor of the first class. For example, if solutions of sodium chloride and cupric chloride are separated by a porous partition and a strip of copper is partly immersed in each, a cell is formed which is capable of generating a current. The E.M.F., however, is very low, and the cell is not a good example of voltaic action.

A cell cannot be formed from three conductors of the first class. For example, if a closed circuit consist of three metals, all at the same temperature, no current flows; and thus, if there are any E.M.F.s at the junctions, they are in equilibrium. From this fact there follows the well-known result of Volta, viz., that the E.M.F. or contact force at the junction of any two metals A, N, is equal to the sum of the contact E.M.F.s in the extended series

$$A/B + B/C + C/D + \dots M/N;$$

supposing additional metals B, C, D,.....M to be included in the circuit between A and N. If it were not so, it would be possible to disturb the equilibrium of a closed circuit consisting of three metals by the introduction of a fourth.

Although such a law has not been verified for liquids, it nevertheless seems improbable that a true voltaic cell could be formed simply from three electrolytes. It is difficult, under these conditions, to see how true electrolytic action could take place. This apparently requires a discontinuity in the circuit, such as is afforded by the change from one class of conductor to the other in the current path.

The question of contact E.M.F. will be considered more particularly later on.

The third condition above mentioned is well exemplified by the voltaic solution of zinc. When zinc is amalgamated, or when it is pure, it is unacted upon by dilute sulphuric acid. But if it is made the positive plate of a closed voltaic couple, solution readily takes place, as we have already seen. In the same way, zinc is but slightly affected by a solution of caustic potash or soda, unless coupled with some electro-negative metal such as iron. Consequently, the fact that a certain reaction does not take place under ordinary circumstances is not a criterion as to whether the same reaction is possible or impossible in a voltaic cell. In fact, a cell will only be efficient if the reaction which it involves does *not* take place under ordinary conditions, i.e., on open circuit.

In the simple voltaic element the liberated ion (referred to in the fourth condition) is hydrogen, which may be regarded as atomic. Atoms being generally incapable of a separate existence, they combine together, and thus hydrogen gas is evolved in the molecular form with which we are familiar. But if a depolariser is present, such as copper oxide, the hydrogen reduces it, combining with the oxygen to form water, and therefore does not appear in a free state. Or it may happen that the hydrogen replaces another ion which is liberated in place of it, as in the Daniell cell, where copper is liberated, although it is not immediately associated with the electro-negative ion which combines with the zinc.

THERMAL RELATIONS IN THE VOLTAIC CELL.—

Electrical energy is produced in a cell as a result of transformation of chemical energy. When a chemical reaction takes place in the ordinary way (not in a voltaic circuit), the energy is liberated in the form of heat; but in the voltaic circuit this heat is mostly transformed and is no longer evolved. Bearing in mind the principle of the Conservation of Energy, we may say that the electrical energy produced by the voltaic solution of a given weight of any element, such as zinc, may, under the most favourable conditions, be equivalent to the heat evolved in the solution of an equal amount non-voltaically.

If a quantity q_0 of electricity flows due to an E.M.F. E , the electrical energy is Eq_0 . For convenience we may take q_0 to be the quantity which is theoretically generated when a gramme atom* of a monovalent element passes voltaically into solution, or which is required for the electrolytic liberation of a gramme atom. Let H be the amount of heat, expressed as work, evolved in the ordinary way upon the formation of a gramme molecule or equivalent of the compound formed by this voltaic solution. Then, if this heat is converted into electrical energy, we must have the following identity: $Eq_0 = H$ or, $E = H/q_0$. This equation, first given by Lord Kelvin, shows the relation, under certain conditions, between the E.M.F. and the heat of formation of the compound voltaically produced.

In addition, however, to a chemical E.M.F., like the above, there may be a thermal E.M.F., as shown by Peltier† effects at the various junctions in the cell, either

* When the atomic weight of an element is regarded as grammes instead of a mere number, the resulting weight is termed the gramme atom. Thus the gramme atom of hydrogen is 1 gramme because its atomic weight is 1; the gramme atom of chlorine is 35.5 because its atomic weight is 35.5. Analogously, the gramme molecule is the molecular weight of a molecule expressed as grammes. Thus the gramme molecule of H_2O is 18 grs.

† When a current of electricity flows across the junction of two metals the junction is heated if the current is in one direction, and cooled if in the opposite direction. This phenomenon is known as the Peltier Effect. Here reference is made chiefly to metal-liquid junctions.

assisting or opposing the chemical E.M.F. In order to arrive at the exact relation between E.M.F. and heat of formation, let us refer briefly to certain thermodynamic conditions.

According to the second law of thermodynamics, continuous work cannot be done by a transference of heat in a system of bodies which are all at the same temperature. Heat energy is present, but it is not available. Given, however, two bodies, one at temperature T and the other at the slightly higher temperature $T+dT$, then a certain amount of work can be done by the flow of heat from the hotter to the cooler body. But this heat cannot be completely transformed into work. As a general principle it may be stated that when a quantity of heat H is brought from a temperature $T+dT$ (on the absolute scale) down to a temperature T , the maximum quantity of this heat which can be transformed into work is not H , but $H \frac{dT}{T}$. For the proof of this statement the

reader must refer to works on thermodynamics, as it would take too long to give the proof here. Since we shall have occasion to refer to this result later on, it will be advisable to clearly bear in mind that

$$\text{work obtainable from heat } H = H \frac{dT}{T}.$$

Now consider the case of a reversible cell, that is one in which the various processes are completely reversed when the direction of the current is changed. This condition is very approximately fulfilled by a Daniell cell containing zinc sulphate and copper sulphate solutions. If a current is generated, zinc is dissolved at one plate and copper deposited at the other. On causing an equal number of coulombs to flow round the circuit in the opposite direction, zinc is deposited and copper is dissolved, the reactions being reversed, though quantitatively equal. Thus the chemical changes and the amounts of heat

corresponding with the reactions are reversible. The Peltier effects are also reversible; but there is one quantity which cannot be reversed, viz., the heat caused by the resistance of the circuit to the flow of current. This depends upon the square of the current, and is therefore independent of the *direction* of the current: heat is always evolved, never absorbed, when it is due to a current flowing through a resistance. But as this heat is proportional to the product C^2R , it may be rendered negligible by making the resistance in circuit large, so that the current is small, and all the thermal effects are then practically reversible.

Let the E.M.F. of a reversible cell be E at some temperature T (on the absolute scale). We may suppose the E.M.F. to be due to a certain chemical heat H_c together with a certain heat H_p of a purely thermo-electric character, so that E is given by the equation

$$E = \frac{H_c}{q_0} + \frac{H_p}{q_0}.$$

To find the value of H_p we will take the cell through the following cycle of operations:—(1) raise its temperature slightly above T , say, to $T+dT$; and (2) allow it to generate q_0 coulombs of electricity. The E.M.F. at the higher temperature will not generally be the same as at T . Let it be $E+dE$. The electrical energy generated is then $q_0(E+dE)$. (3) Now allow the cell to cool down to T ; and (4) pass q_0 coulombs in the opposite direction (*i.e.*, in opposition to the E.M.F.). The electrical energy necessary for this operation is q_0E .

The cell is now in its original state. The heat that was required to raise the temperature to $T+dT$ was recovered upon cooling; and the chemical changes, which give rise to the direct current, are reversed by the charging current, for the cell is by hypothesis reversible. Now, in the second operation the cell gave energy amounting to $q_0(E+dE)$ to the external circuit, and in the fourth

operation energy to the extent of $q_0 E$ was returned to the cell. Hence the external circuit has actually gained energy amounting to

$$q_0 (E + dE) - q_0 E = q_0 dE.$$

This is the case every time the cycle of operations is completed. Consequently, the cell is able to furnish an endless supply of energy by continuing these operations.

But, since the chemical processes are each time reversed, this energy is not due to the chemical E.M.F., which is practically the same at the two temperatures. It must, therefore, be due to the term H_r which we have called the thermo-electric heat. The energy gained is not, however, simply equivalent to this heat; for, as we have already seen, such heat is not wholly available.

We must, therefore, write

$$H_r \frac{dT}{T} = q_0 dE,$$

from which we have

$$H_r = q_0 T \frac{dE}{dT}$$

as the required value of H_r . The equation for E now becomes, by substitution,

$$E = \frac{H_c}{q_0} + T \frac{dE}{dT}.$$

This most important equation was first given by Helmholtz.

The reader may feel some doubt as to whether the heat H_r really falls from the temperature $T + dT$ down to T , i.e., whether the necessary heat is absorbed by the *hot* cell; for, it will be observed, the energy in the cycle of operations was restored to the cell at the *lower* temperature. That such is really the case may be seen by considering two cells, at the two different temperatures, coupled up in opposition to each other. Such a system will give a current so long as the difference in temperature is maintained, notwithstanding the fact that the total chemical E.M.F. is zero. The energy is, therefore, supplied

PRIMARY BATTERIES.

the thermo-electric E.M.F. If the necessary heat is absorbed at the lower temperature it would only be necessary to surround the hot cell with a non-conducting jacket in order to produce perpetual motion. Consequently, the heat must be absorbed at the higher temperature. If the hot cell has a lower E.M.F. than the cold one the current is a reversed one through the hot cell, heat is still absorbed at the higher temperature. If a cell has an E.M.F. higher than that which is equivalent to the chemical reactions it must absorb heat in generating a current, and evolve heat when a reverse current is passed, and *vice versa*.* If the E.M.F. does not vary with the temperature, or has no temperature-coefficient it is called, it is then given simply by the heat of formation and the Helmholtz equation reduces to the simpler form given by Kelvin. But this is very seldom the case.

The above equation H_e is expressed as work, not as heat. For our purpose, however, we shall find it more convenient to have this quantity expressed in calories.† When that is so, let it be represented by H ; $H_e = JH$, where J is the mechanical equivalent of

Thus

$$E = \frac{JH}{q_e} + T \frac{dE}{dT}.$$

J is equal to 42 million ergs, and q_e is equal to 4.8 coulombs, or 9,654 C.G.S. units of electricity. We therefore have

$$E = \frac{42 \times 10^6}{9,654} H + T \frac{dE}{dT}, \text{ in C.G.S. units;}$$

Expressing E in volts,

$$\begin{aligned} E &= \frac{4.2}{96,540} H + T \frac{dE}{dT} \\ &= \frac{H}{23,000} + T \frac{dE}{dT} \text{ volts.} \end{aligned}$$

* further, Cantor Lectures on Electro-Chemistry by J. Swinburne, Royal Society of Arts, 1896.

† calorie is the amount of heat required to raise one gramme of water 1°C. to 5°C.

If the temperature coefficient is zero and the E.M.F. unity, we see that $H = 23,000$. In other words, in order that a chemical reaction should give rise to one volt in a voltaic circuit it must, under ordinary chemical conditions, evolve 23,000 heat units, or calories, per gramme equivalent of the compound formed.

Generally, when considering the thermal relations in voltaic cells, we have to deal with bivalent elements, such as zinc, cadmium, copper, &c. The equivalents of monovalent metals are equal in value to their atomic weights; but, in the case of bivalent elements, the equivalents are only half the atomic weights. Thus a gramme equivalent of hydrogen is 1 (the atomic weight being 1); but a gramme equivalent of zinc is $\frac{65.5}{2}$ (the atomic weight being 65.5). To avoid the inconvenience of dividing by 2, it is preferable to remember that the number of calories equivalent to one volt in the case of bivalent elements amounts to 46,000, in which case the equation becomes

$$E = \frac{H}{46,000} + T \frac{dE}{dT} \text{ in volts,}$$

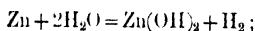
H being here used to indicate the heat evolved when a gramme atom of a bivalent element enters into combination, or when two gramme atoms of a monovalent element likewise enter into combination.

When the E.M.F. diminishes with rise of temperature $\frac{dE}{dT}$ becomes negative, and must be subtracted from the purely chemical part of the equation instead of being added.

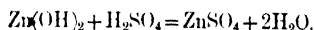
This equation has been obtained on the assumption that the cell is reversible, but there is no reason why it should not be applicable to cells which are irreversible with regard to the chemical reactions. Reversibility has nothing to do with the generation of the current, although

an irreversible reaction completely changes the effect of a reverse current.

Let us now consider one or two examples of the calculation of the chemical part of an E.M.F. In a simple element, consisting of zinc and platinum in dilute sulphuric acid, zinc sulphate is formed when a current is generated. As to whether this salt is formed by the direct union of metal and acid radicle, or whether the metal is first oxidised and then dissolved, as stated by early physicists, is of no consequence. The result is the same from the thermochemical point of view. According to the older idea we have



and then



The final products are zinc sulphate and hydrogen. Although two molecules of water are broken up in the first equation, they are re-formed in the second. Thus the quantities of heat relating to the water cancel out, and we have simply the heat of formation of zinc sulphate, such as results on dissolving the metal in sulphuric acid of the strength used in the cell. The heat of formation of a gramme molecule of this salt, using dilute sulphuric acid, is 37,730 calories, and consequently the E.M.F. is

$$\frac{37,730}{46,000} = 0.82 \text{ volt.}$$

It is found that a single cell of this kind will not decompose water (acidulated) under ordinary conditions. This is readily understood when it is remembered that the heat of formation of water is 68,400 calories per gramme molecule. Thus the E.M.F. necessary to effect decomposition is greater than

$$\frac{68,400}{46,000} = 1.49 \text{ volta.}$$

Let us now transform our simple element into a Daniell cell, containing zinc in dilute sulphuric acid and copper in a solution of copper sulphate.

In this case, also, when a current is generated, zinc sulphate is formed, but hydrogen is no longer liberated. The latter reacts electrolytically with the copper sulphate, and copper is deposited instead of hydrogen, as indicated

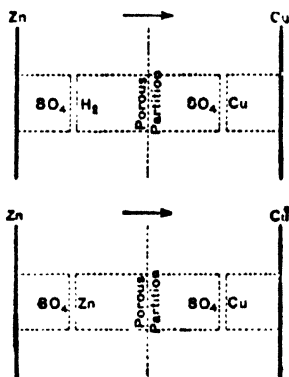
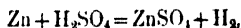
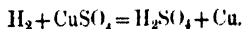


FIG. 15.—Reactions in a Daniell Cell.

in the top diagram of Fig. 13. We have not only the reaction



but also that expressed by the equation



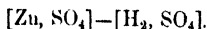
The heat of formation of zinc sulphate, as already stated, is 37,730 calories. Now the solution of copper by dilute sulphuric acid does not take place unless heat is applied. In fact, the heat of formation of copper sulphate in this way is negative, being equal to -12,400 calories: the reaction is what is termed endothermic. But in a Daniell cell the reverse reaction takes place. This is, therefore,

exothermic and evolves heat to the above extent. Consequently, the use of copper sulphate as a depolariser in a Daniell cell raises the E.M.F. above that of a simple element by an amount corresponding to 12,400 calories, the total chemical E.M.F. being

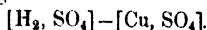
$$\frac{37,730 + 12,400}{46,000} = \frac{50,130}{46,000} = 1.09 \text{ volts.}$$

From this it appears that, if the addition of a depolariser is to cause an increased E.M.F., it must be of such a nature that the reaction with the polarising ion is exothermic.

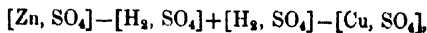
This cell may also be regarded in a slightly different way. Expressing the heats of formation of gramme molecules in the usual manner,* we may represent the heat evolved by the formation of zinc sulphate (from Zn and SO_4) together with the breaking up of sulphuric acid as follows:



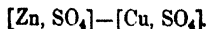
In the other reaction, consisting in the formation of sulphuric acid and the breaking up of copper sulphate, we have the following:



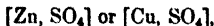
Thus, for the complete reaction, we have heat to the extent of



or, simply,



That is, the chemical E.M.F. is due to the difference in the heats of formation of zinc sulphate and copper sulphate. We do not know the thermal value of the reactions



* An expression, such as $[\text{Zn}, \text{O}_2, \text{SO}_2]$, indicates the heat evolved when a gramme molecule of a compound is formed from the constituents included in the brackets.

but, as we are only concerned with the *difference* in the heat of formation of two similar salts, we may take some other method of formation in our calculations, provided the same method is taken for both salts. Thus we know, from the work of Thomsen, that

$$\bullet \quad [\text{Zn, O}_2, \text{SO}_2] = 177,420 \text{ calories,}$$

$$\text{and} \quad [\text{Cu, O}_2, \text{SO}_2] = 127,290$$

Therefore

$$\begin{aligned} [\text{Zn, SO}_4] - [\text{Cu, SO}_4] &= [\text{Zn, O}_2, \text{SO}_2] - [\text{Cu, O}_2, \text{SO}_2] \\ \bullet \quad &= 50,130 \text{ calories;} \end{aligned}$$

whence the value of the E.M.F. is seen to be the same as before.

It will be noticed that these calculations are independent of the sulphuric acid. No sooner is one molecule of the acid decomposed than another is formed, and thus the corresponding quantities cancel. Consequently, any other suitable sulphate, besides that of hydrogen, may equally well be used. In practice, a solution of zinc sulphate is employed, in which case the reactions are those indicated in the lower diagram of Fig. 13, p. 49.

In these examples, only the chemical part of the E.M.F. has been considered. When the law was first given by Lord Kelvin, the thermal part was not included, and, consequently, the calculations based upon the theory were not well supported. The fact that a purely thermal term enters into the calculation of the E.M.F. from thermochemical data, rendering it impossible to complete such calculations merely from the latter, has too often been disregarded by writers upon this problem. In the case of the Daniell cell the temperature coefficient is very small, and thus its effect upon the E.M.F. may be neglected. But, in general, the thermal term is considerable.

As a verification of the Helmholtz equation the following results are of interest. They are deduced

from the work* of Jahn* upon a number of reversible cells of the Daniell type :—

Nature of Cell.	$\frac{dE}{dT}$	
	In volta.	E.M.F. in volta.
Cu, CuSO ₄ + 100H ₂ O ZnSe ₆ + 100H ₂ O, Zn	+ 0.000034	1.0975 1.0962
Cu, CuC ₂ H ₃ O ₄ , Aq PbC ₂ H ₃ O ₄ + 100H ₂ O, Pb	+ 0.000385	0.4940 0.4764
Ag, AgCl ZnCl ₂ + 100H ₂ O, Zn	- 0.000409	1.0429 1.0306
Ag, AgCl ZnCl ₂ + 50H ₂ O, Zn	- 0.000210	1.0085 1.0171
Ag, AgCl ZnCl ₂ + 25H ₂ O, Zn	- 0.000202	0.9687 0.9740
Ag, AgBr ZnBr ₂ + 25H ₂ O, Zn	- 0.000106	0.8383 0.8409
Ag, AgNO ₃ + 100H ₂ O Pb(NO ₃) ₂ + 100H ₂ O, Pb	- 0.000632	0.9336 0.9320
Ag, AgNO ₃ + 100H ₂ O Cu(NO ₃) ₂ + 100H ₂ O, Cu	- 0.000708	0.4587 0.4580

The Helmholtz equation shows us that the E.M.F. of a cell is limited by the heat of the reaction involved; and it is for this reason that E.M.Fs. have not been obtained much higher than 2 volts. Although there are many reactions which correspond to a higher pressure, unfortunately they are not available voltaically. It might be thought that a higher E.M.F. could be obtained by having reactions, as it were, in series, just as the E.M.F. of a simple cell is raised by having copper sulphate in circuit and thus converting the cell into a Daniell. The depolariser undoubtedly adds energy to the combination. But the addition of another solution in a porous pot between the zinc sulphate and the copper sulphate would produce little or no effect on account of the decompositions which must accompany the formation of every compound at the surfaces of separation of the electrolytes.

APPARENT EXCEPTIONS TO THE HELMHOLTZ EQUATION.

—A good deal of care is necessary in calculating the E.M.F. from thermo-chemical data, for reasons we will very briefly consider. In the first place, we assume that a certain chemical reaction takes place in the cell in question; but this reaction may in reality be considerably modified. For example, films of sub-salts may form upon

* *Wied. Ann.*, Vol. 28, pp. 21-43 and 491-497.

the plates; or the electrolyte may contain dissolved gases, which combine with gases that are formed voltaically. On that account the E.M.F. observed by means of an electrometer, or when only a very small current is required, may differ from that which is found when a considerable current is being generated (apart from polarisation effects), the latter value corresponding with the normal chemical reaction.

Secondly, the thermo-chemical data are obtained by the interaction of substances in the ordinary state, whereas electrolytically deposited or reduced metals may be materially different. Care must always be taken to ensure that the thermal data taken do really correspond with the reactions that are assumed. Heats of dilution must also be taken into account. The care that is necessary is well shown in the many investigations on the E.M.F. of the lead accumulator as calculated from such data.

Thirdly, thermo-chemical data cannot be accurately determined, and therefore calculations based upon them should be accepted with some caution. For example, the heat of reaction of lead acetate and zinc is given respectively by Thomsen, Favre, and Andrews as 34,950, 31,200 and 37,710 calories.

THE TEMPERATURE COEFFICIENT AS A THERMO-ELECTRIC EFFECT.—Before leaving the subject of the thermal relations that are to be found in the voltaic cell, it will be of interest to consider the temperature coefficient a little more from the thermo-chemical point of view. We have so far looked upon this variation of the E.M.F. as due to a Peltier effect. If that is really the case, it is reasonable to suppose that the change of E.M.F. per degree is the algebraic sum of variations of E.M.F. at the various junctions. The mean variation of E.M.F. of a thermo-electric couple at any temperature, or $\frac{dE}{dT}$ is

known as the thermo-electric power of the couple. The above supposition may therefore be expressed by saying that the temperature coefficient of the cell is equal to the sum of the thermo-electric powers at the junctions.

Experiments have been made by Bouty, and also by Carhart, which verify this statement. In a Daniell cell, for example, there are three contacts, viz.:—zinc/zinc sulphate, zinc sulphate/copper sulphate, and copper sulphate/copper. Carhart investigated the two metal/liquid junctions, and obtained results which are graphically shown in Fig. 14. Here the ordinates represent the

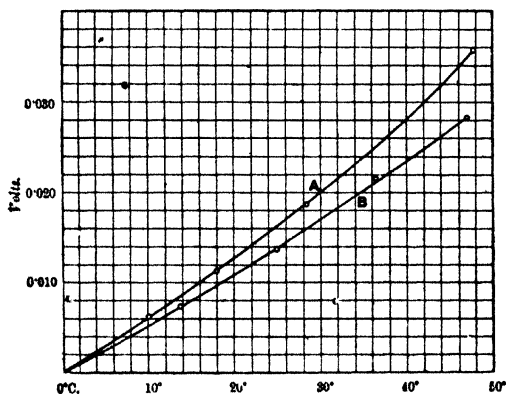


FIG. 14.—Curves showing the E.M.F. of thermo-couples at the metal/liquid junctions in a Daniell Cell.

variation of E.M.F., and the abscissa the corresponding temperature of the hot junction, the cold junction being at 0°C. Curve B shows the increase of E.M.F. when the Cu/CuSO₄ junction of an experimental Daniell Cell was heated, the Zn/ZnSO₄ junction being kept at 0°C. Curve A shows the decrease of E.M.F. (plotted for convenience as an increase) when the Zn/ZnSO₄ junction was heated. These curves are nearly the same as those obtained for the

two single thermo-couples Cu/CuSO_4 and Zn/ZnSO_4 . The thermo-electric powers of the latter were found to be 0.00073 and 0.00079 respectively. Now, in a Daniell cell these are opposed to each other. Consequently, neglecting the zinc sulphate/copper sulphate junction, the effect of which appears to be very small, the sum of the thermo-electric powers amounts to $0.00079 - 0.00073 = 0.00006$ volt per degree. The change of the E.M.F. per degree of a modified Daniell cell was found by Carhart to be 0.000073 volt. The agreement is not very exact, but is sufficiently close to support this method of regarding the matter.

Let us now pass on to a brief consideration of the chief theories that have been put forward to account for voltaic action.

THE CHEMICAL AND CONTACT THEORIES.—Volta, as already mentioned, found that the muscular movements observed by Galvani were also produced on connecting two parts of the same muscle by an arc of two metals. He therefore came to the conclusion that a junction of dissimilar metals was necessary in such experiments, and that the force which gives rise to the observed phenomena, and to voltaic phenomena generally, is due simply to the contact of the metals. According to this theory, the E.M.F. of a cell consisting of, say, zinc and platinum in dilute sulphuric acid, is due merely to the junction of zinc and platinum. In support of the contact theory, as it is called, Volta constructed a dry pile, which has already been described, and he also carried out a number of electrostatic experiments.

One of the most important results obtained may be stated as follows:—If a condenser be made of two plates of different metals, such as zinc and copper, which are connected for an instant by a piece of zinc or copper rod (i.e., by one of these two metals), the condenser becomes charged. On separating the plates, the leaves of a gold

leaf electroscope connected to one of them diverge, giving a measure of the charge and of the force giving rise to it. By observing the divergence, and by carrying out measurements with different metals, Volta found the contact force to be definite for any given couple, and he was able to place the metals in a series, such that any metal is electropositive to all those following it in the series. Thus zinc is electropositive to iron and iron to copper. He also demonstrated the fact, known as Volta's law, that, if there is a series of contacts, the contact forces are additive. For example, indicating the contact force of a copper-zinc junction by Cu/Zn , then, in the case of iron, or any other metal, we have the relation

$$\text{Cu/Fe} + \text{Fe/Zn} = \text{Cu/Zn}.$$

This fact is illustrated in the adjoining diagrams. Fig. 15 represents a condenser having copper and zinc plates, connected by zinc and copper strips. The force is due to

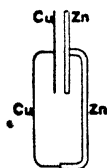


FIG. 15.—Contact Force.

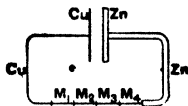


FIG. 16.—Contact Force.

the junction of the latter. In Fig. 16 a series of metals, M_1, M_2, M_3, M_4 , is also included in the circuit. The force is now the sum of all the contacts, thus:

$$\text{Cu/M}_1 + \text{M}_1/\text{M}_2 + \text{M}_2/\text{M}_3 + \text{M}_3/\text{M}_4 + \text{M}_4/\text{Zn}.$$

But, in accordance with Volta's law, this is simply equal to the contact Cu/Zn . In fact, in an open circuit, which the above is practically equivalent to, the force is due merely to the end metals, being independent of inter-

mediate ones. If the circuit were closed we should have

$\text{Cu}/\text{M}_1 + \text{M}_1/\text{M}_2 + \text{M}_2/\text{M}_3 + \text{M}_3/\text{M}_4 + \text{M}_4/\text{Zn} + \text{Zn}/\text{Cu}$,
which reduces to

$$\text{Cu}/\text{Zn} + \text{Zn}/\text{Cu}.$$

Assuming that the force from copper to zinc is equal and opposite to that from zinc to copper, we have

$$\text{Cu}/\text{Zn} = -\text{Zn}/\text{Cu},$$

or

$$\text{Cu}/\text{Zn} + \text{Zn}/\text{Cu} = 0,$$

i.e., the total force in the closed circuit is zero. This is found experimentally to be true, provided the temperature of the circuit is uniform throughout.

In reviewing the Contact Theory from the historical point of view, it must be remembered that the Law of the Conservation of Energy was not brought forward until long after the beginning of the present century, and therefore the absurdity of supposing that the mere contact of two metals could give rise to a continuous flow of electricity was by no means self-evident. There was, on the other hand, a good deal of evidence in favour of such an idea. Even the phenomenon of electrolysis observed in fluid cells could, without much difficulty, be regarded as an effect rather than the cause of the current, and thus, indirectly, as an effect due to the metallic junction.

That chemical action invariably takes place in a voltaic circuit was very soon proved by the opponents of the Contact Theory, who therefore concluded that all the observed phenomena were due to chemical action, and that contact force was a negligible quantity, or non-existent. As already mentioned in Chapter I, a very lengthy dispute arose between the supporters of the Contact and Chemical Theories.

CONTACT FORCE.—Let us now consider a little more carefully the nature of Volta's contact force. Unfortunately, even after the lapse of a century, scientific opinion

is still divided upon the question. This remark must, indeed, be extended to the whole theory of the voltaic cell; and therefore the reader should bear in mind that the opinions here expressed do not necessarily embody the only views that are of value: no theory at present put forward can be considered as more than a working hypothesis open to a good deal of adverse criticism.

Lord Kelvin has given an elegant experimental proof of the existence of contact force. A light metallic electrified needle A (see Fig. 17) is suspended over a metal disc, which is divided into two halves in contact with each other. When these are of the same

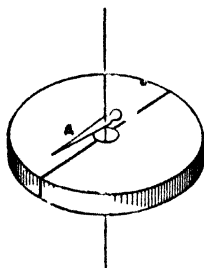


FIG. 17.—Kelvin's Bimetallic Disc Experiment.

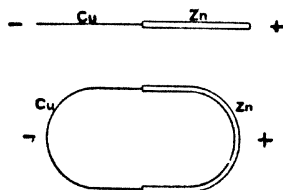


FIG. 18.

metal, say copper, and are placed symmetrically with regard to the needle, the latter is not deflected, however highly it may be charged. But if one of the copper segments is replaced by one of zinc, a deflection occurs. When the charge is positive, the needle deflects towards the copper; when it is negative, the deflection is towards the zinc, thus showing that the zinc is positive to the copper. In this experiment the needle should be maintained at a high potential, which is most readily effected by connecting it to a highly charged Leyden jar. The metal segments may be connected by a wire, or they may be placed directly in contact, or even soldered together:

the result is always the same. But if the segments are slightly separated, and are then connected by a drop of water instead of by a piece of wire, the needle is no longer deflected. This result has been taken to indicate that there is no contact force between metals and water, but later research has shown that a small contact force does exist.

When speaking of contact E.M.F. it is well to remember that the effect is purely statical, and differs materially from an E.M.F. which gives rise to a continuous current. If a piece of copper, Cu (Fig. 18), is joined metallically to a piece of zinc, Zn, the latter is charged positively and the former negatively on account of the contact E.M.F. But no current flows on completing the circuit, however that may be done, because an equal and opposite contact E.M.F. is introduced by so doing. The zinc still remains positive and the copper negative, as indicated in the figure. It will, therefore, readily be seen that all measurements of contact force must be of a statical kind, involving the use of a condenser or some equivalent arrangement.

Now let us consider more particularly the measurement of contact force. Kohlrausch, who carried out a large number of such measurements, made use of an air condenser, having its plates of the metals whose contact force was to be measured. An insulated plate of platinum, for example, is supported opposite and parallel to an insulated plate of zinc, the distance between them being comparatively small. The plates are connected for an instant by means of a wire of any convenient metal. Let Pt, Zn, in Fig. 19, be the plates, and Cu the connecting wire. Then the contact force acting is: $\text{Zn/Cu} + \text{Cu/Pt} = \text{Zn/Pt}$, which is what we wish to measure. The plates become charged, by reason of the contact force, with a certain quantity of electricity, and, therefore, when the connection is broken, the plates remain at different potentials. The object in view is to obtain a measure of

this potential difference. If the two plates are next connected to the terminals of an electrometer, the latter becomes charged. Now the quantity of electricity on the plates of a condenser is equal to the product of the capacity into the potential difference, or, in the form of an equation, $Q = KV$. If Q is constant, as in the present instance, V must vary inversely as K . By the introduction of the electrometer, the capacity of the system is increased. Consequently, the potential difference is decreased, and the deflection on the instrument may be too small to be of any value. But if the platinum and zinc plates are separated, the capacity is much diminished, and thus the potential difference at the terminals of the electrometer is increased sufficiently to give a much larger deflection than would otherwise result.

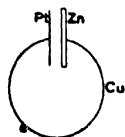


FIG. 19.—Charging of a Condenser by Contact Force.

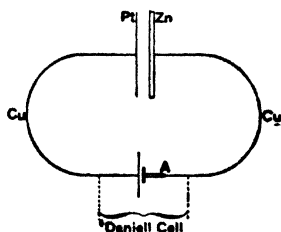


FIG. 20.

The deflection thus obtained is a measure of the so-called contact force. If a plate of copper, of the same size, is substituted for the platinum and precisely equivalent operations are carried out with the copper-zinc condenser, as are described above for platinum and zinc, a different deflection is observed on the electrometer, giving a measure of the contact force Zn/Cu . The actual value, in volts, of the electrometer reading may be found by making both plates of the condenser of the same metal, charging them to a known difference of potential by

means of a Daniell or other suitable cell, and observing the deflection upon separating the plates as before. In this way, contact forces between different pairs of metals may not only be compared, but their actual value may be determined. It is here assumed that the capacity of the condenser is the same in all measurements. This condition, however, is not easy to fulfil accurately. By the substitution of one metal for another it may happen, for example, that the distance between the plates does not remain quite the same, or, perhaps, the area is somewhat different. To avoid errors of this kind, Kohlrausch introduced a Daniell cell into the circuit used for connecting the condenser plates, by which means the value of the contact force is obtainable in terms of the E.M.F. of this cell as follows:—

Let α be the deflection of the electrometer when a simple wire is used to connect the plates, as already described. Since α is proportional to the charge, and thus to the contact force giving rise to it, we may write

$$\text{Zn/Pt} = k\alpha, \quad \dots \dots (1)$$

where k is a constant. Now include a Daniell cell, whose E.M.F. is E , in the connecting wire, as shown in Fig. 20. It must be remembered, in estimating the contact forces here in action, that the contact at A, of the zinc plate of the Daniell with the copper wire, must be included in the cell, because the E.M.F., E , necessarily includes this contact. In fact, the cell, to be complete, must have both poles terminating with the same metal, say copper: this is not actually the case in practice, but the closing of the circuit by any metal is equivalent to it. Thus the total E.M.F. is given by

$$\begin{aligned} & \text{Zn/Cu} + E + \text{Cu/Pt} \\ &= \text{Zn/Pt} + E, \end{aligned}$$

and, if β is the deflection observed, we have

$$\text{Zn/Pt} + E = k\beta. \quad \dots \dots (2)$$

The value of Zn/Pt is now obtainable in terms of the E.M.F. of the Daniell by eliminating k . Thus, by substituting in equation (2) the value for k given by equation (1), we have

$$Zn/Pt + E = Zn/Pt \frac{\beta}{\alpha}.$$

Therefore,

$$\begin{aligned} Zn/Pt &= \frac{-E}{1 - \frac{\beta}{\alpha}} \\ &= E \frac{\alpha}{\beta - \alpha}. \end{aligned}$$

In this way the value of a contact force is obtained in terms of a known E.M.F. A direct comparison between contact forces is avoided, and it is only necessary to maintain the capacity constant during measurements of any given pair of metals, which is comparatively easy. Whether an alteration is introduced in the capacity on changing from one metal to another is immaterial, so long as the contact force to be measured is referred in every case to the Daniell cell.

Lord Kelvin, in measuring contact force, employed a null method, which will be understood on referring to Fig. 21. The two plates under observation, which are represented by Zn and Cu, are placed at a small distance apart and are connected to a quadrant electrometer E. If they are metallically connected they become charged by the contact force, and if they are separated, after this connection is broken, a deflection of the electrometer results. But if the charge upon the plates could be exactly neutralised, by an E.M.F. equal and opposite to the contact force, no deflection would occur. This can be readily effected by the arrangement indicated in the figure. Current from a battery B flows through a resistance RR', along which a sliding contact S can be placed in any desired position. Thus the potential difference between S and R' can be varied. If then

contact be made at P, there is a circuit from one plate to the other, and this circuit can be made to include a potential difference acting in opposition to the contact force, and tending to neutralise the charge upon the plates. When the slider is adjusted so that the charge is neutralised, i.e., so that no deflection occurs on separating the plates, then the potential difference between S and R' is equal to the contact force.

Hankel, Pellat, Brown, Pfaff, Von Zhan and many others have carried out measurements upon contact force. The most complete experiments were made by Ayrton and Perry,* the principle of whose method we will briefly

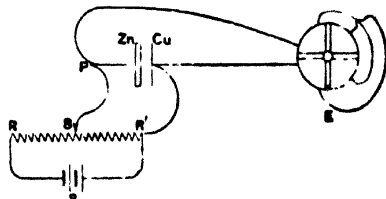


FIG. 21.—Kelvin's Null Method of Measuring Contact Force.

describe. Referring to Fig. 22, A and B are two plates of the metals under observation, metallicly connected; C, D are two gilt brass plates connected to the terminals of a quadrant electrometer: they are parallel to A, B, and at a definite distance from them. A, B, by reason of the contact force between them, are charged—one positively and the other negatively. There will, therefore, be charges induced upon C and D. The latter are at first metallicly connected together and earthed. In this way the free charges are removed (the plates C, D being of the same metal), and a zero reading of the electrometer is taken, after which these plates are insulated from each other and from earth, but remain connected to the

* *Proc. Royal Soc.*, Vol. XXVII., p. 197, and *Phil. Trans.*, 1880, Part I., p. 15.

electrometer. A and B are now interchanged, A being placed below D and B below C, the distances being precisely the same as before. The deflection of the electrometer, when this is done, is a measure of the contact force. Although the principle of the method is simple, the actual apparatus is intricate and requires careful adjustment.

Contact forces also exist between metals and liquids, and between different liquids. These can all be measured by the method of Ayrton and Perry. For this purpose the liquid under observation is held in a basin and the surface is brought into the position A in Fig. 22. If the contact force between this liquid and a metal is to be measured, the latter is placed, as before, at B, contact being made by a strip of the same metal attached to the plate and dipping into the liquid. The contact force between two liquids may be measured by having one at A

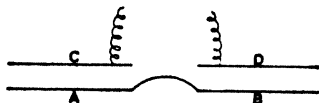


FIG. 22.—Ayrton and Perry's Method of Measuring Contact Force.

and the other at B. In that case contact is made by means of a siphon tube closed at each end by a membrane and filled with one of the solutions: this tube is allowed to dip into the two basins.

With regard to metal-liquid and liquid-liquid junctions, it is found that the apparent contact forces do not often obey Volta's law. This is not altogether surprising. When two metals are placed in contact, no chemical reaction as a rule takes place; or, if there is a reaction, it is generally far too minute (with the exception of mercury) to be observed, unless it be allowed to continue for weeks. But when a metal is immersed in a liquid, chemical change of an electrolytic nature may take place with

comparative ease, and thus it is not surprising that the E.M.F. in a closed circuit, such as zinc/neutral potassium chloride/mercury/zinc, is not zero.

In the same way, changes may take place at liquid junctions owing to chemical reactions and to diffusion. To prove the failure of Volta's law in the case of liquid junctions, Fechner* dipped identical metal plates M, M (Fig. 23) into two vessels containing the same liquid, L. These vessels he placed in communication, by means of moist cotton wicks, with two others containing different liquids L_1 , L_2 . If Volta's law applies to the liquid junctions, there should be no current upon closing the



FIG. 23.—Fechner's Experiment on the Application of Volta's Law to Liquid Junctions.

circuit, because the metal-liquid junctions are equal and opposite. The condition that no current should flow is in fact

$$M/L + L/L_1 + L_1/L_2 + L_2/L + L/M = 0;$$

or

$$L/L_1 + L_1/L_2 + L_2/L = 0.$$

Experiment shows that a current *does* flow in such a case, and therefore it is said that Volta's law is not obeyed. But such junctions cannot be looked upon as equivalent to those between metals. Diffusion is taking place at each junction, and a number of diffusion cells are really formed, as will be described in Chapter VI., and thus the resultant E.M.F. cannot, as a rule, be zero.

We have so far tacitly assumed that contact forces do not exist between gases and metals or liquids. Unfortunately, their existence has not been proved, but that is no reason for entirely disregarding them. In measuring the contact force of copper to zinc, for example, what we really determine is the sum

$$\text{air / copper} + \text{copper / zinc} + \text{zinc / air},$$

* *Pogg. Ann.*, Vol. 48, pp. 1 and 125, 1839.

and this we generally term simply the contact force, Cu/Zn. This in no way affects the additive nature of these forces. In the case of a platinum copper contact, for example, we have

air / platinum + platinum / copper + copper / air,

and if this be added to the above expression for a copper / zinc contact we have

air / Pt + Pt / Cu + Cu / Zn + Zn / air = air / Pt + Pt / Zn + Zn / air,

the other terms cancelling. This expression is what is regarded as Pt/Zn.

The question as to whether gas-effects really exist cannot be decided by measurements in vacuo or in different gases, because any variations so obtained in the E.M.F. may be equally accounted for by supposing that a change occurs in the contact force of the two metals themselves.

So far we have assumed contact force to be of the nature of an E.M.F. As to whether we are justified in so doing depends to a large extent upon the way in which we define our terms. E.M.F. is often regarded as the force which gives rise to the current. But as a current can only be obtained through the transformation of some other form of energy, it is preferable to say that an E.M.F. not only gives rise to the current, but is accompanied by a transformation of energy; and thus when we say that there is an E.M.F. at a certain point in a circuit, we mean that a transformation into electrical energy of some other form of energy is taking place at that point. For instance, at a thermo-electric junction, heat is being transformed into electrical energy; and in a dynamo, mechanical energy is likewise being transformed. A clear distinction, however, must be drawn between potential difference and E.M.F., as already mentioned. In a shunt from a main circuit, it might be said that the current is due to the potential difference at the terminals of the shunt, and that there is no such transformation between those points. But this

potential difference is in reality due to the current, and thus to the E.M.F. in the main circuit.

Accepting this view of electromotive force, we may say that when a current flows past a point where an E.M.F. exists, then work is done of two kinds—reversible and irreversible. The work done by reason of the E.M.F. is reversible, depending upon the direction of the current; but the work done in heating the conductor depends upon the square of the current and is therefore irreversible. Consequently, when a current encounters an E.M.F. work is done which may be positive or negative according to the direction. For example, if a current flows in accordance with the E.M.F. at a thermo-electric junction, heat is there absorbed; if it flows against the E.M.F., heat is evolved. We may go further, and say that the measure of an E.M.F. at any point is given by the reversible work done when a unit of electricity is conveyed past the point. Thus, if W is the work done when Q units of electricity flow past a point, the E.M.F. at that point is given by

$$E = \frac{W}{Q}.$$

It should be remarked that this statement, although generally accepted in reference to a complete circuit, has not been universally admitted when it refers to only part of a circuit.

Now, when a current traverses the junction of two metals, the well-known reversible thermo-electric Peltier effect arises. Being reversible, it indicates an E.M.F. which we may, perhaps, be permitted to call the true contact E.M.F. The value so obtained is very much smaller than the corresponding contact force of Volta and is sometimes in the opposite direction.

It has been stated by Pellat and others that the Peltier effect has no connection with contact force. The argument put forward is somewhat as follows:—When two bodies A , B are in contact, they are at different potentials, this potential difference V being due to, equal to, and opposit

to, the contact force E . Thus, when a current passes, there are two Peltier effects: one for E and the other for V . Since these are equal and opposite, they cancel, any inequality giving rise to the Peltier effect that is actually observed. Lodge* has pointed out that a fallacy arises from the assumption that what is only proved for the whole circuit is true for the junction.

Accepting, therefore, the statement that the true contact E.M.F. is small, how shall we regard Volta's contact force, which is about one hundred times as great? Lodge prefers the view that, when two metals are placed in contact, they are at the same potential, but differently charged; and that they form practically an air battery, the charges resulting through oxidation.

Consider, for example, a piece of copper and a piece of zinc at some distance apart in air. The molecules of oxygen may be looked upon as striving to attack both the metals. Now, when a compound is formed voltaically, the corresponding E.M.F. is proportional to the heat evolved in the formation of this compound from the same constituents non-voltaically. Thus the E.M.F. due to the oxidation of copper would be proportional to the heat of formation of copper oxide. We may suppose that charged atoms are trying to move up to the metal. They are unable to do so because they are straining equally on all sides, and if they did so it would lead to a charge of one kind of electricity without a compensating opposite charge on some other conductor. But if we assume that atoms which are unable to combine exert the same attraction as those which are on the point of combining with the metal, then we may consider it probable that the copper is at a lower potential than the air, the difference being proportional to the heat of combustion of copper. In this way it may be calculated that the copper is at a lower potential than the air by about 0.8 volt and the zinc by about 1.8 volta.

* B.A. Report, 1884, p. 464.

As soon as the metals touch they are reduced to the same potential, and are no longer completely surrounded by oxygen atoms. These latter can now move nearer to the zinc, because a way of escape is provided for the electricity into the copper. This electricity is negative, oxygen being electronegative. The inward motion of the atoms towards the zinc diminishes what we may regard as the thickness of the layer of the negative electricity on this metal, whereas the thickness of the layer on the copper is increased. Consequently, the zinc is charged positively and the copper negatively. Although the potential is the same throughout (viz., the mean of the initial potentials, if the plates are of the same size, *i.e.*, 1.3 volts in this case), there is a slope of potential in the air. In considering the system as a condenser, the air surfaces close to the metals must be regarded as the two coatings of the condenser, and the potential difference between them amounts to the difference of the two initial potentials, in this case 1.8 - 0.8, or 1 volt. It is the charge of one of the plates which is measured by the ordinary condenser methods, although indirectly the above potential difference is determined.

Lodge gives the following table, showing to what extent the calculated values agree with experiment. The alternative numbers are due to uncertainties in the thermochemical data :—

Volta Effects in Air.

Metal Pairs.	Calculated from heat of Combustion.	Observed by				
		Pellat.		Ayrton and Perry.		Clifton.
		Clean.	Scratch'd.	Com- mercial Zinc.	Amalga- mated Zinc.	—
Zinc—						
Tin.....	0.39	0.25	0.35	0.28	0.46	...
Lead	0.70 or 0.65	0.15	0.31	0.20	0.35	...
Iron	0.21 or 0.4	0.56	0.70	0.60	0.74	0.75
Nickel ...	0.23	0.47	0.63
Copper ...	1.04 or 0.9	0.71	0.86	0.75	0.89	0.85
Mercury...	1.18	1.06	1.20	1.07
Silver.....	1.71 or 1.58	0.91	1.12

It is, however, a little difficult to see how a metal can be brought to a definite potential below that of the air, depending upon the heat of combustion, when no combination is able to take place. Moreover, a voltaic reaction with an elementary gas is improbable. It would seem simpler to suppose a difference of potential to be brought about by voltaic oxidation through films of moisture or otherwise.

Several observers have attempted to attack this idea of oxidation by showing that measurements in vacuo do not exhibit such differences from those at ordinary pressures as would be expected if this theory were true. Von Zahn found that contact force was not appreciably changed by different gases or by variation of pressure, except in the case of a zinc-platinum junction. The value of the latter fell to half a Daniell in vacuo.

Bottomley* found that the value of zinc/copper remained the same when the pressure was reduced to $2\frac{1}{2}$ millionths of an atmosphere, and also when hydrogen was substituted for air. The apparatus employed in this investigation was such that a variation of one per cent. would certainly have been detected.

More recently, J. R. Erskine-Murray† replaced air by paraffin wax, the plates of zinc and copper being filed under melted wax so as to remove any air films that might be present. The difference in the contact force due to this replacement of air by wax amounted to only 0.053 volt.

Experiments by J. Brown‡ upon a copper-zinc condenser, which was maintained in an atmosphere of nitrogen under reduced pressure and in the presence of metallic potassium for as long as seven and a half years, also gave negative results. The contact force was found to be much the same as in air.

* B.A. Report, 1885, pp. 901, &c.

† Proc. Royal Soc., Vol. 63, pp. 113, &c., 1898.

‡ Proc. Royal Soc., Vol. 64, pp. 369-374, 1899.

These experiments, however, are not so conclusive as might appear at first sight. The capacity of two plates such as are used in the measurement of contact force is very small, and consequently the quantity of electricity required to charge the condenser so formed is also very small. Suppose the surface of each plate to be 10 sq. cms., and that their distance apart at the moment of charge is 0.1 mm. The capacity is then $\frac{1}{1.13 \times 10^{10}}$ farads, and the number of coulombs required to charge this system to a potential difference of one volt amounts to the same figure. The weight of oxygen corresponding to this quantity is 0.0734×10^{-10} milligrammes. This quantity is so small that it might be present many thousand times over without our being able to detect it. The necessary reaction might still take place in the best vacuum, or even under paraffin wax. We should, however, expect the speed of the reaction to be much less than in air, in the same way that a dry pile can only supply electricity slowly owing to the limited chemical action. Results of interest might therefore result by determining whether the rate of charge varies as the pressure is reduced.

The interpretation of experiments carried out in different gases is a difficult matter because we have to distinguish between voltaic action and ordinary chemical action. If gases are used which react easily with either of the metals, the results are liable to be of little value owing to the films formed upon the metals. Hydrogen sulphide, for example, gives trouble on this account. An experiment with this gas, carried out by Brown,* may be mentioned here in support of chemical action. A Kelvin bimetallic disc of iron and copper, enclosed in a glass jar, was used for observing the contact force. When hydrogen sulphide was admitted, the deflection was

* *Phil. Mag.*, 5th Series, Vol. 6, p. 142, 1878.

seen to reverse and to remain reversed until the copper became covered with sulphide, which has no affinity for sulphur, when the deflection became uncertain.

With a view to completely changing the medium around the contact, and the thorough removal of gaseous films from the surfaces of the metals under test, a careful investigation has been carried out by F. S. Spiers.* An attempt was first made to remove these films by heating the couple *in vacuo*, but oxidation by the residual atmosphere was the only result. The air was therefore replaced by hydrogen, the couple being platinum-aluminium. But nevertheless it was found that "even in a high vacuum of pure, dry hydrogen at the minute pressure of $1 \frac{1}{1000}$ mm. of mercury, and after four washings in that gas, there is still sufficient oxygen present to completely oxidise the surface of an aluminium plate if it be only brought to a sufficiently high temperature." Finally it was decided to remove the air films chemically by heating in hydrogen, a platinum-iron couple being used. The glass containing-tube was washed out four times with hydrogen, and then heated a number of times to about 800°C . A steady value was not easily obtained, but the final result was that the contact force fell from $+0.37$ to -0.60 volt, which Spiers regards as the true value of the Volta effect between iron and platinum in an atmosphere of hydrogen. On admitting a small quantity of air the E.M.F. slowly varied towards a positive value, and on heating to accelerate the change it rose to $+0.22$ volt. Further heating reduced this figure to zero owing to oxidation.

This conclusion assumes that we are really dealing with the metals in an atmosphere of hydrogen. It is doubtful, however, whether the Volta effect actually observed is not between hydrides of the metals instead of the metals themselves. In fact a crucial experiment demonstrating the absence of films appears to be impossible. Even at the

* *Phil. Mag.*, Vol 49, pp. 70-80, Jan., 1900.

ordinary temperature in air, films of oxide, of air, or of moisture must be assumed, until they can be disproved, and, if they are removed in any way they are merely replaced by others.

A point of considerable interest, brought out by the researches of Pellat, and also by those of Erskine-Murray, is that the value of the contact force depends upon the mechanical state of the metallic surfaces. Thus burnished zinc was found by the last-named author to fall 0.32 volt when scratched by polishing on glass paper. The results of Pellat were in the opposite direction, but the surfaces in his case were washed with alcohol. It thus appears that a closed metallic circuit, including two zinc-copper junctions, instead of being in equilibrium, may have a resultant E.M.F. of 0.32 volt if the junctions are in different mechanical states, even though at the same temperature.

Lord Kelvin* concludes, from this result of Erskine-Murray's, that the potential in zinc "increases from the interior through the thin surface layer of a portion of its surface affected by the crushing of the burnisher, more by 0.32 volt than through any thin surface-layer of portions of its surface left as polished and scratched by glass paper." It does not, however, appear wholly impossible that the molecular change brought about by burnishing should bring about a corresponding change in the chemical affinity; but we should rather expect a *decreased* electrification in such a case to arise from burnishing.

Of a similar nature are the experiments of N. Hessehus,† which tend to show that the physical condition of the surface has an important effect. This investigator found that a polished surface was in all cases positive with respect to a matt surface of the same substance. It would seem, however, that such an effect is susceptible of a chemical

* *Phil. Mag.*, 6th Series, Vol. 6, pp. 82-120, 1898.

† *Jour. Russk. Chimikov*, 1902; "Science Abstracts," Vol 5, No. 1.087 (1902).

explanation. A matt surface is likely to be acted upon more quickly by gases than a polished surface, and if we bear in mind that an oxide is electro-negative to the metal of which it is formed, it follows that a matt surface should be electro-negative to one of the same metal that is polished. This view receives some support from the work of H. Beil,* who traced certain variations of contact force in the case of freshly cleaned zinc to the action of water vapour.

An investigation by de Broglie† is on somewhat similar lines. This physicist found that when metals were placed in a drying chamber the contact potential, which was normally in the neighbourhood of one volt, dropped to a few hundredths of a volt. This would tend to show that the contact force is chiefly due to films of moisture, rather than hydroxide on the surface, for mere drying would not remove oxide.

Q. Maiorana‡ has found that low temperatures reduced the contact force to a marked extent. Thus the contact force between zinc and gold, which in air is 0.88 volt, drops to 0.05 volt when liquid air is dropped on the junction. The conclusion is reached that at the absolute zero of temperature the contact force would vanish. This effect may be regarded as supporting a chemical basis of contact potential.

All these investigations show the extreme difficulty there is in devising conclusive experimental investigations on which a really definite theory may be based.

It has been suggested that contact force may be due to chemical affinity between the metals. If that were so, the force should be equivalent to the heat of formation of the alloy formed from the two metals. Thus the contact force of zinc and copper should be given by the heat of formation of brass. Very few thermo-chemical data of this kind exist, but the figures given by Kelvin show that

* *Annalen der Physik*, Vol. 31, p. 849, 1910; "Science Abstracts," Vol. XIII., No. 852 (1910).

† *Comptes Rendus*, Vol. 152, p. 696, 1911; "Science Abstracts," Vol. XIV., No. 657 (1911).

‡ *Nuovo Cimento*, Vol. 12, p. 196; "Science Abstracts," Vol. IV., No. 652 (1901).

the heat evolved on the formation of brass is very much below the equivalent of the contact force.

Some determinations of this kind have also been made by J. B. Tayler,* who measured the heat of amalgamation first of the alloy and then of its constituents. Assuming that the products are the same in the two cases, the difference in the heats of amalgamation gives the heat of formation of the alloy. Experiments were made with various alloys and a number of different percentages. Where the percentage is such as to give a large gramme molecule, the heat of formation may equal, or even surpass, the equivalent value of the contact force. But the fact that an alloy of a certain percentage has a heat of formation equivalent to the contact force can only be looked upon as a coincidence unless we have reason to believe that this particular alloy is really produced when a current flows across a contact of the two metals in question.

SEAT OF THE E.M.F.—The controversy caused by the contact and chemical theories died out as the doctrine of the conservation of energy sprang into existence. Since electrical energy must of necessity be obtained by the transformation of some other form of energy, it could not be produced by contact alone. But another controversy arose which has not yet been brought to a satisfactory conclusion. Admitting that contact force exists and that chemical action is also necessary, what point in the circuit may we regard as the seat of the E.M.F.?

Consider a simple element consisting of zinc and copper in dilute sulphuric acid. When the circuit is closed there are three contacts, viz., Zn/Cu, Cu/acid, and acid/Zn. Owing to the comparatively large value of the contact force between copper and zinc (about 0.75 volt) and the small values of the contact force for the other two

* *Phil. Mag.*, Vol. 50, pp. 37-43, July, 1900.

junctions, it is somewhat natural to assume that the seat of the E.M.F. is at the copper-zinc junction. The value of the contact force, however, is not quite as high as the actual E.M.F. of the cell, and there is no obvious reason why the other two contacts should be left out of account. Possibly their exclusion is due to the idea given by Kelvin's divided-disc experiment, that when zinc and copper are placed in water they are at the same potential. But it has been shown by Ayrton and Perry* that, although this may be true at the instant of immersion, the zinc soon becomes negative to the copper, and thus the total E.M.F. becomes greater than the value of the contact force at the metallic junction. The same authors have shown that the E.M.F. of a cell is equal to the sum of all the contact forces in the circuit. The E.M.F. cannot depend upon the metallic junction only, for it would then be independent of the electrolyte, which is not the case. Another objection to placing the E.M.F. at this junction arises from the fact that no apparent change takes place there. It is natural to expect a change somewhere, and if we accept the idea that energy must be transformed where an E.M.F. exists, it becomes necessary to look to some other part of the circuit.

Passing on to the two acid junctions, we find that the contact force in both cases is small. At the surface of the platinum, hydrogen is evolved, but otherwise no other chemical change takes place: the platinum remains unaffected. At the surface of the zinc, on the other hand, there is a marked chemical change, the metal being dissolved, and, therefore, the zinc/acid junction is generally favoured as the seat of the E.M.F. by those who accept the definition of E.M.F. given above. It is not clear, however, why the platinum/acid junction should be left out of consideration. The ordinary solution of zinc by sulphuric acid involves the formation of zinc sulphate and

* *Proc. Roy. Soc.*, Vol. 27 p. 196, 1878.

the liberation of hydrogen at the same spot. But when the solution is effected electrolytically the salt is formed at one plate, whilst the hydrogen is liberated at the other and there is no reason why the energy corresponding to the reaction should not be partly transformed at one plate and partly at the other. Taking the whole circuit into consideration it seems more reasonable to say there are three seats of E.M.F., viz., at the junctions zinc/acid, platinum/acid, and zinc/platinum, the latter being very small.

Various other views have been stated from time to time. For instance, Fleeming Jenkin* has expressed the opinion that the E.M.F. is probably due to the metallic junction, but that the current, which is maintained by it, is produced by chemical action.

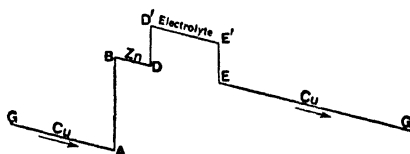


FIG. 24.—Variation of Potential in a Voltaic Circuit, according to Ayrton and Perry.

Ayrton and Perry† prefer to say that, although energy is transformed at the zinc plate, a potential difference, equal to the contact force, exists at the metallic junction. In support of this view they give a representation, which is reproduced in Fig. 24, of the variation of potential in the circuit. The broken line here given is supposed to be continuous, the two points marked G being one and the same. The current is flowing in the direction of the arrows, and potential is measured upwards. The zinc part of the circuit is represented by BD, the electrolyte by D'E', and the copper by EGA. The circuit being closed, there is a fall of potential along the conductors,

* "Electricity and Magnetism," 7th Edition, p. 55.

† *Phil. Mag.*, Vol. 21, p. 51, 1886.

and therefore the lines representing them are given a sloping direction. At the junction of copper and zinc there is a rise of potential indicated by A B. Similarly at the zinc/acid junction there is a rise, shown by D D', and at the acid/copper junction a fall, shown by E' E. Making use of the usual hydraulic analogy, we may imagine a pump to be working somewhere in D' E'. The water, in circulating, gains potential energy wherever it rises: thus potential energy is gained in rising from A to B and from D to D' (these parts being supposed to be vertical); but no external energy is there supplied, the pump being in D' E'. In other words, the place where energy is transformed (by the pump) is not necessarily the place where potential energy is gained. Similarly, in the actual

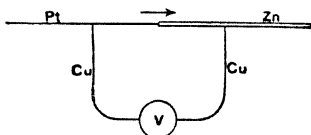


FIG. 25.

circuit, energy is transformed at the zinc/acid junction, but there may be a rise in potential at the zinc/platinum junction. A distinction is thus drawn between E.M.F. and potential difference which is not easy to understand.

It might be thought that such a potential difference, if it really existed, could be readily detected by means of a voltmeter connected to each side of the junction, as indicated in Fig. 25. But, in such a case, the junction effect appears twice and neutralises itself. Suppose the voltmeter V to be wound with copper and to be connected up with copper; then the total potential difference acting upon the instrument is:—

$$\begin{aligned}
 & \text{P.D. due to current} + \text{Pt/Zn} + \text{Zn/Cu} + \text{Cu/Pt} \\
 &= \text{P.D. due to current} + \text{Pt/Zn} + \text{Zn/Pt} \\
 &= \text{P.D. due to current.}
 \end{aligned}$$

Hence the effect observed is due to the current only, and is independent of the junction. The same remark applies to an electrostatic instrument. Let the inductor be of some metal or alloy M, as indicated in Fig. 26. Then, beginning at the left-hand side of the instrument, we have, as the total E.M.F. acting,

$$\begin{aligned} & \text{M/Cu} + \text{Cu/Pt} + \text{P.D. due to current} + \text{Pt/Zn} + \text{Zn/Cu} \\ & \qquad \qquad \qquad + \text{Cu/M} \\ & = \text{Cu/Pt} + \text{P.D. due to current} + \text{Pt/Cu} \\ & = \text{P.D. due to current.} \end{aligned}$$

This difficulty, which occurs equally at a metal liquid junction, is at once overcome if we assume the definition of E.M.F. already given, and thus accept measurements

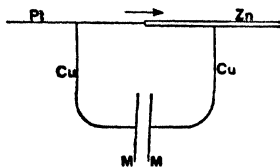


FIG. 26.

of the Peltier effect. These indicate only a small E.M.F. at a metallic contact, and large values at the metal-liquid junctions. But then it is a matter of definition.

Swinburne* has made the bold assertion that there is no seat of the E.M.F., and that a coulomb of electricity in flowing round the circuit formed by a closed cell continually falls in potential, never regaining it. This view of the matter is best explained by considering a magnetic circuit. Suppose we have a horseshoe electro-magnet, or a ring magnet with an air gap in it. Imagine a "unit pole" near one of the magnet poles. Let it move over to the other pole. The work which it does in so

* See Cantor Lectures on "Electro-Chemistry," by James Swinburne, *Journal of the Society of Arts*, 1896.

moving is a measure of the difference of magnetic potential between the magnet poles. Let it move on through a small tunnel in the iron until it regains its first position; the additional work done is of the same sign as before. Thus each time the unit pole moves round the magnetic circuit, a definite amount of work is done, which we know to be equal to $0.4\pi nc$, where n is the number of turns in the magnet winding and c the current in amperes flowing through them. Each time the unit pole moves round this path, its circuit is interlinked with the electric circuit and the same amount of work is done. It therefore follows that the magnetic potential at any point has an infinite number of values differing by multiples of $0.4\pi nc$.

Consider, further, a conductor in the form of an incomplete ring through which a magnetic pole is being moved. An E.M.F. is generated in the ring, giving rise to a potential difference, which we may suppose equal to one volt, at its terminals. If a coulomb is allowed to flow from one terminal to the other, it falls in potential and does work to the extent of one joule. If it continues to flow along the conductor, it still does work of the same sign, owing to the resistance of the conductor and consequent variation of potential. Thus, in passing round the circuit to the terminal from which it started, the coulomb does a certain amount of work, say, two joules. Every time it passes round the circuit it does work to the same extent, and so it follows, as in the case of the magnetic circuit, that each point in the conductor has an infinite number of potentials. This statement is not opposed to the usual definition of potential, viz., that the potential of a point on a conductor is equal to the work done in moving unit quantity of electricity up to that point from an infinite distance, because there is no stipulation as to the path to be followed by this unit quantity; it might follow the most direct path, or it might

pass several times round the circuit under consideration, thus increasing the work done.

Now consider a cell, the external resistance of which is infinitely large compared with the internal resistance. Suppose the potential difference at the terminals to be one volt. Unit quantity of electricity in passing from the positive to the negative terminal falls one volt in potential: the work done amounts to one joule as before. If the electricity passes on through the cell to the other pole the additional work done is negligible; but, such as it is, it corresponds with a further fall of potential. People generally have the idea that the potential is again raised in passing through the cell, but Swinburne prefers to think that it still falls and that there is a cyclic difference of potential just as there is in the magnetic and electric circuits already described.

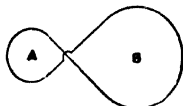


FIG. 27.

The analogy does not, however, seem altogether clear. There certainly are cases, even where the E.M.F. is due to variation of induction, in which there is what may be regarded as a seat of E.M.F.; for example, a dynamo, connected to an external circuit, is the seat of E.M.F. for that circuit. Again, suppose we have a conductor bent into the form of a figure 8, as in Fig. 27. Let a magnet move through the part A, and let B be completely shielded from induction, which is theoretically possible. As the magnet moves, an E.M.F. is generated in the loop A, but not in B. Thus it would not be unreasonable to look upon the loop A as the seat of E.M.F. for the entire circuit. Theoretically, A might be as small as we please and thus the seat of E.M.F. would be located at one point of the circuit.

In coming to the voltaic cell, it is not easy to see how a cell is strictly similar to the electric circuit with which it is compared. The latter is cutting the lines of force throughout the whole length as the magnet moves, and the E.M.F. results through the relative motion of two bodies which are entirely independent of each other. There is no reason why one point rather than any other of the conductor should be looked upon as the seat of the E.M.F. But in a cell the case is very different. The circuit is, as it were, self contained. The E.M.F. is not in any way dependent upon a body external to the circuit, and thus it is not unnatural to place the seat of E.M.F. at one of the junctions, or points of discontinuity.

Those interested in the theory of the Voltaic cell should read the presidential address delivered in 1900 by Lodge* to the Physical Society of London, in which the whole subject is discussed.

CONCLUSIONS WITH REGARD TO THE SEAT OF ELECTROMOTIVE FORCE.

—Perhaps the safest conclusion to which a consideration of the various theories lead is that the whole matter is largely a question of definition, and that it is, therefore, of relatively very small importance. It depends a great deal upon the point of view, and so we cannot say that one theory is correct and another necessarily wrong. This statement is also true of many other phenomena, as pointed out by Willard Gibbs.† For example, some people might say that the circulation of water in a hot-water system is due to the action of gravity upon the vertical columns of water at different temperatures and having different densities; others might say that it is due to the furnace.

Our ideas are naturally based upon processes most familiar to us. Being accustomed to the flow of water

* "Proceedings," Physical Society, Vol. XVII., p. 359. *Phil. Mag.*, Vol. 49, pp. 351-383 and 454-475, 1900.

† *Electrical Review*, Vol. 15, p. 407, Nov. 22, 1894 (Discussion on Lodge's Paper on "The Seat of Electromotive Force," B.A.).

under the action of gravity, we are struck with the similarity of electric flow, and thus we are tempted to carry the analogy too far. It is convenient to think of electricity being raised in potential at some point in the cell, just as a pump raises water to a higher level, keeping up a continuous stream and enabling the water to do work by its downward flow. But the pump is not necessarily placed where the water gains potential energy. We may, of course, define the seat of E.M.F. as the point where energy is given to the circuit, but that is only a definition, and we cannot always decide upon the position of such a point.

CHAPTER V.

THEORY OF THE VOLTAIC CELL (*continued*).

Electrolytic Mechanism of the Voltaic Cell, p. 83.—Objections to the Grotthus Theory, p. 83.—Modification of Clausius, p. 86.—Ionisation Theory of Arrhenius, p. 88.—Electrolytic Conductivity, p. 89.—Osmotic Pressure, p. 91.—Vapour Pressure, p. 94.—Boiling Point and Freezing Points of Solutions, p. 96.—Behaviour of Electrolytes, p. 97.—Osmotic Pressure Theory of Cells, p. 99.—Electrolytic Solution Pressure, p. 99.—Calculation of a Single E.M.F., p. 100.—Measurement of a Single E.M.F., p. 105.—Calculation of Electrolytic Solution Pressure, p. 108.—Influence of Negative Ion, p. 109.—Comparison of the Helmholtz and Nernst Equations, p. 110.

ELECTROLYTIC MECHANISM OF THE VOLTAIC CELL.

—Let us now pass on from the various discontinuities of the voltaic circuit to a consideration of what takes place within the electrolyte itself. We know that a certain decomposition takes place, and that certain compounds are formed, but how shall we imagine conduction to be carried on? What, in fact, is the mechanism of conduction?

In Chapter II. an account was given of the theory of Grotthus. This theory is in accordance with the broad facts of electrolysis, but in the following respects it has been found wanting:—

1. LIMITING E.M.F. NECESSARY FOR DECOMPOSITION.—We should expect the E.M.F. to exceed a certain limiting value, according to this theory, before electrolytic decomposition could take place. But, in certain cases,

this is not found to be so. For example, the application of the smallest E.M.F. to two copper plates immersed in the solution of a copper salt will cause a current to flow. If we suppose conduction to take place by means of Grotthus chains, we should expect no current to flow until the applied E.M.F. is equivalent to the heat of formation of the compound in solution. It would then be capable of decomposing a molecule in the chain, and recompositions and decompositions would follow according to the hypothesis. That no such limiting E.M.F. is found to be necessary has been explained by saying that the energy required for any decomposition is returned to the circuit by the immediate recomposition which follows, as already explained. Such a statement, however, leads to a second difficulty.

2. VIOLATION OF THE SECOND LAW OF THERMODYNAMICS.—The recomposition which follows a decomposition no doubt returns energy to the circuit, and in this way the *total* energy expended in a given time might be nil. But we cannot admit that a decomposition can be due to a subsequent recomposition, or that work can be done by energy which is given to the system after the work which it accomplishes is complete. Such a statement would be a direct contradiction of the second law of thermodynamics, which practically affirms that energy in a state of rest cannot of itself become active.

3. REPLACEMENT OF A BOUND BY A FREE ION.—It is sometimes objected that the successive decompositions in a Grotthus chain take place through the replacement of a combined ion by a free ion, and that there is no reason why such a replacement should take place. That is no doubt the case if each ion is looked upon as really free after the decomposition of its molecule. But, in reality, the ions cannot very well be regarded in

such a light, as they are under the influence of electric forces throughout.

4. MIGRATION OF THE IONS.—When electrolysis takes place, the ions move towards their respective electrodes bearing their charges with them. In a Grotthus chain we have the equivalent of two streams of ions, moving in opposite directions, and apparently with the same velocity. Now if a current is passed through a solution of copper sulphate by means of platinum electrodes, it is found that more copper sulphate is lost about the cathode than about the anode. This phenomenon, which

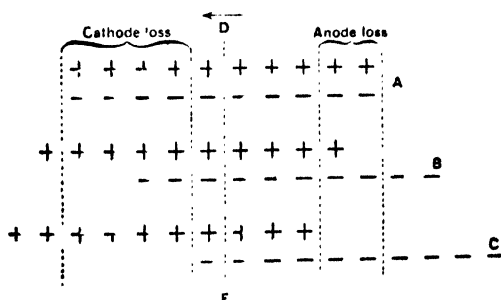


FIG. 28. — Migration of the Ions.

is a very general one in electrolysis, was explained by Hittorf on the assumption that the velocities of the two ions are different. In the case of copper sulphate, for example, if the Cu ion travels more slowly than the SO_4 , the effect would be equivalent to a bodily transfer of CuSO_4 towards the anode, and would account for the observed phenomenon. These apparently unequal migration velocities, as they are called, are generally considered as evidence against the theory of Grotthus.

The migration of the ions will be more readily understood by referring to Fig. 28. Here each positive ion is

represented by a plus sign, and each negative ion by a minus sign.

At the start, each positive ion has a negative one alongside it, as indicated on the line A. Suppose the negative ions to move twice as fast as the positive. Then when three ions have been deposited, the positive ions have moved one space to the left and the negative ions two spaces to the right, as indicated on line B. Line C shows the state of things when six ions have been liberated. Now if we imagine the cell to be divided into anode and cathode compartments by the line DE, we see that the loss at the cathode is double that at the anode, just as the velocity of the anion is double that of the cation. The ratio of the velocities (on the assumption that there is no transfer of electrolyte or hydration of the ions) is given by the ratio of the losses of the compound in the neighbourhood of the two electrodes.*

Such losses might, however, be accounted for by supposing that the ions, although moving with equal velocities, are often complex, carrying molecules of the solution along with them. It is also not impossible to imagine unequal velocities of the ions in a Grotthus chain. After the recombination of a molecule has taken place in a chain of this kind, it will be noticed, according to the usual representation, that the molecule is facing the electrodes in the wrong way. It is therefore necessary for a rotation to take place. The two ions will rotate about their centre of mass, and, if their masses are not equal, it follows that the motion of one ion in one direction will be greater than that of the other ion in the opposite direction. Consequently the ionic velocities will be different, and the observed concentration-changes will follow as a matter of course.

MODIFICATION OF CLAUSIUS.—Owing to the somewhat unsatisfactory nature of the Grotthus hypothesis, Clausius introduced the idea that the ions of any molecule are not

* See S. W. J. Smith (*Proc., Phys. Soc.*, Vol. XXVIII., p. 143, 1916) on the incompleteness of this explanation.

always linked to one another, but that they are continually exchanging partners, as it were, with the ions of the other molecules. For example, in a solution of sodium chloride, the sodium and chlorine of any molecule do not for long remain attached to one another; the sodium changes place with the sodium of a second molecule and the chlorine may change place with the chlorine of a third molecule. This interchange is continually going on, so that a certain number of free ions are always in solution. In the ordinary state of things the direction of motion of the free ions is in no definite direction. But as soon as an E.M.F., however small, is applied at the electrodes, the free ions move along the lines of force and collect at the electrodes, where they will separate if the E.M.F. is sufficient to overcome the polarisation and prevent recombination. Voltaic action is also readily explained, in the manner suggested by Helmholtz, if we assume that each metal (or electrode) has a specific attraction for electricity, and consequently for the ionic charges. Thus it would be assumed that zinc attracts a negative charge more powerfully, and a positive charge less forcibly, than does copper. Consequently when plates of copper and zinc are placed in sulphuric acid, there is a resultant attraction of the positive hydrogen towards the copper and an attraction of the negative SO_4 towards the zinc. As the ions interchange they will be drawn, under the influence of these forces, to one or other of the attracting plates, where they will be deposited. On open circuit, however, such deposition will soon cease, because each plate will become positively or negatively electrified and the resulting electrostatic charge will repel those ions in solution which are of the same sign, and thus prevent their further deposition. In this way, the zinc will become negatively, and the copper positively, electrified. Since the ionic charges are large the amount of chemical action necessary to bring about this electrification is very

minute; but upon closing the circuit chemical action continues, because the charges on the two plates neutralise each other, giving rise to a current, and more deposition can then take place. The simple Grotthus theory does not allow such a spontaneous electrification, but otherwise it permits an explanation on somewhat similar lines.

IONISATION THEORY.—Clausius, as we have seen, assumed that a certain small proportion of ions were in the free state. In 1887 Arrhenius went a step further and asserted that practically *all* the molecules of an electrolyte in dilute aqueous solution are dissociated, or ionised, as it is called, into charged ions, any undissociated molecules being electrolytically inactive. Thus, when sodium chloride is dissolved in water the solution contains very few molecules, these being nearly all broken up into free Na and Cl. The solution does not look yellow or smell of chlorine because chlorine, as we know it, is Cl_2 , not Cl, and for a similar reason the sodium ions do not decompose the water. But when the ions become deposited and separated from their charges, then they are transformed into the molecular condition to which we are accustomed. Nevertheless, the idea that a stable salt like sodium chloride should be resolved into its constituent atoms simply by dissolving in water is at first sight somewhat difficult to understand. On that account, and also because of the great importance of the theory, not only in electrolysis but also in primary cells, we shall do well to see upon what foundations it is based. These foundations are chiefly concerned with electrolytic conductivity, osmotic pressure, vapour pressures of solutions, and boiling points and freezing points of solutions. It would take too much space to consider these subjects fully, and we shall therefore only attempt to give a very brief account of each, simply in its relation to solution and the theory of ionisation.

ELECTROLYTIC CONDUCTIVITY.—Kohlrausch made a large number of measurements of the conductivity of electrolytic solutions. Specific conductivity, or the reciprocal of the resistance between opposite faces of a one-centimetre cube of the solution, gives very little insight into the question of dependence of conductivity on concentration. If the conductivity depends upon the concentration of the solute rather than upon the solvent, the latter should be more or less eliminated from a statement of results from which a law of any kind is expected to follow. For this reason Kohlrausch made use of what is termed **molecular conductivity** which is obtained numerically by multiplying the specific conductivity by the volume, in cubic centimetres, containing one gramme molecule of the substance in solution. If a number of substances are taken and a solution of each is made up containing one gramme molecule per litre, the number of molecules in unit volume of each solution is the same, and the conductivities are therefore comparable. One litre is generally taken as the unit of volume in such measurements, and therefore when a solution contains one gramme molecule per litre, the molecular conductivity is 1,000 times the specific conductivity. If a solution of this strength is diluted, the molecules become more separated, and the specific conductivity cannot be compared with that previously observed. But on multiplying this conductivity by the new volume, this separation of the molecules is compensated for, and we obtain a measurement of the molecular conductivity which is comparable with the previous value. If the specific conductivity varied inversely as the volume, the molecular conductivity would remain constant, but that is not the case.

Kohlrausch obtained two very remarkable results. The first may be stated as follows:—The molecular conductivity of an electrolytic solution increases with the dilution and reaches a maximum value approximately corresponding with infinite dilution.

The following figures, which refer to a solution of potassium chloride and are due to Ostwald, afford an illustration of this fact:—

Gramme equivalents per litre.	Molecular conductivity.	Percentage of Molecules ionised.
3.0	879	68
1.0	977	75
0.5	1,018	78
0.1	1,113	86
0.03	1,178	90
0.01	1,219	94
0.006	1,235	95
0.001	1,268	98
0.0006	1,275	98
0.0001	1,285	99
Infinite dilution.	1,296	100

Here the molecular conductivity increases with the dilution, tending towards a maximum, which is reached when the dilution is infinite. If we regard molecular conductivity as a measure of ionisation, then this maximum corresponds with a state of complete ionisation; and the ratio of the molecular conductivity at any concentration to that at infinite dilution gives the percentage of molecules ionised at that concentration, as shown in the right hand column of the above table.

Secondly, Kohlrausch found that a change of cation produces a definite change of molecular conductivity independent of the anion in very dilute solution, and the same is true for a change of anion. For example, the difference in molecular conductivity between equimolecular dilute solutions of KCl and NaCl is equal to the difference between solutions of KNO_3 and NaNO_3 of the same molecular concentration. From this it follows that the molecular conductivity at infinite dilution consists of the sum of two independent terms, which depend upon the anion and cation respectively, and which may be taken as being equal to the ionic velocities. In the form of an equation we have

$$\mu_{\infty} = u + v,$$

in which μ_{∞} is the molecular conductivity at infinite dilution and u, v , the ionic velocities. The statement that the velocities of the ions are independent of one another is known as the Law of Kohlrausch. Solutions of normal salts having two monovalent ions are found to obey this equation closely, but the molecular conductivities in the case of polyvalent ions are smaller than would be expected. It is, therefore, preferable to take Ostwald's modified form of the equation, and to include a constant α such that

$$\mu_x = \alpha(u + v).$$

Under what may be regarded as normal conditions α is unity and the equation reduces to the simpler form.

The above facts were known at the time that Arrhenius brought forward his theory, and they formed some foundation upon which to build it. If we accept the idea of independent ionic velocities, the entire independence of the ions themselves at once suggests itself. We will now pass on to work which was completed at a later date and which has served to strengthen and confirm the theory of ionisation.

OSMOTIC PRESSURE.—The nature of osmotic pressure will be most readily understood by referring to the following simple experiment. In Fig. 29, the vessel A is the head of an inverted thistle funnel, the stem being broken off. Across the top is stretched a piece of bladder which is tied round the funnel. In order to make a water-tight joint, the bladder should first be made wet with hot water so as to obtain an even surface, after which it is slightly dried. The funnel is made hot, and some Chatterton insulating compound is quickly applied all round the edge. While the Chatterton is still hot the funnel is placed top downwards upon the bladder, which is then tied round the edge. If properly carried out, a perfectly water-tight joint will result. When the vessel so formed is complete, it is filled nearly to the top of the neck with a strong

solution of sugar, and joined by a good fitting piece of rubber tubing B to a fine capillary glass tube C. By slowly pushing the latter down into the vessel A, the level of the sugar solution in the capillary tube may be adjusted to any desired height. The vessel A is now immersed in a beaker of water D. For the first hour or two very little may happen. Possibly the level in the capillary tube will even fall. But at the end of a day, a

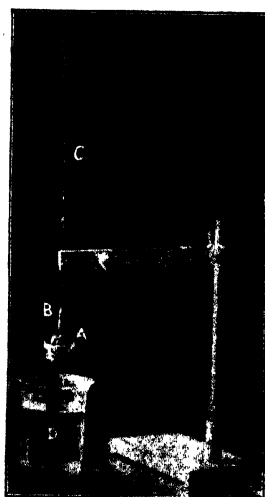


FIG. 29. — Osmotic Pressure.

very decided rise will be observed due to what is termed the osmotic pressure of the sugar. As soon as the diaphragm assumes a steady state the rise is rapid. With a tube of about half a millimetre bore and a funnel $1\frac{1}{4}$ in. diameter, the author has observed a rise of 11cm. in twenty minutes.

This pressure is generally explained by saying that the sugar molecules are striving to pass through the

membrane into the water. The membrane acts like a molecular filter, being impermeable to the sugar molecules, but permeable to the water molecules; and so the water passes inwards, but there is little or no exit of sugar if the membrane is suitable. Various membranes are employed in experiments of this kind, artificial ones being the most effective.

The pressure so observed, which may amount to several atmospheres, is generally regarded as the pressure exerted by the sugar molecules. On observing the osmotic pressures of various solutions it is found that equimolecular solutions exert equal osmotic pressures, thus showing that the pressure depends upon the number of the molecules in solution per unit volume. This result is similar to the law of Avogadro for gases, which states that equal volumes of gases measured under the same temperature and pressure contain the same number of molecules.

As the result of a number of experiments, Pfeffer found that the osmotic pressure of a solution is proportional to the concentration and to the absolute temperature. Now, the concentration of a solution is the reciprocal of its volume. We may therefore write this result in the form

$$P = R' \frac{1}{V} T,$$

or

$$PV = R'T,$$

in which P is the osmotic pressure, V the volume, R' a constant, and T the absolute temperature.

Van't Hoff was the first to point out the striking analogy between this result and the laws of Boyle and Charles, which are embodied in the well-known equation referring to gases, viz. :—

$$pv = R'T,$$

in which the letters have similar significations to those in the previous equation, the only difference being that in

the former we are dealing with a volume of solution, whereas in the latter a volume of gas is in question. Upon investigating the results of Pfeffer, van't Hoff found that the values of the constants R and R' in the two equations were practically the same, whence he came to the following remarkable conclusion:—The osmotic pressure exerted by the molecules of a given weight of substance in solution is equal to the pressure which an equal weight of the substance would exert at the same temperature if it occupied a volume in the gaseous state equal to that of the solution.

It thus appears that a substance in solution (at least when *dilute*) acts in the same manner as a gas, and that the laws of Avogadro, Boyle and Charles all apply to such solutions if the osmotic pressure be substituted for the gaseous pressure. It is therefore concluded that, in the process of dissolving, a substance breaks up to a very large extent into separate molecules. When the solution is sufficiently dilute all the molecules assume a separate existence, and the osmotic pressure then becomes a measure of the number of molecules present. Such, briefly, is van't Hoff's theory of solutions. Before discussing the bearing of this theory on ionisation, we will pass to other results which serve to confirm this view.

VAPOUR PRESSURE.—When a liquid is placed in a confined space, evaporation takes place, and continues until the vapour exerts upon the walls of the enclosure a definite pressure varying with the temperature. This fact can be easily shown by introducing a drop of liquid into the vacuum^{*} above the mercurial column of a barometer. The level of the mercury falls, and this fall, supposing the lower level of the mercury to remain practically constant, is a measure of the vapour pressure.

^{*} The more recent work of Morse, Lord Berkeley and others has shown that the correspondence is more exact if the concentration is referred to the volume of the solvent instead of to that of the solution.

Now if a liquid contains a body in solution it is found that the vapour pressure of this solution is less than the vapour pressure of the pure liquid. By working with solutions in this way, Raoult arrived at the following conclusions:—

1. If p is the vapour pressure of the solvent and p' that of the solution, then the relative depression $\frac{p-p'}{p}$ is independent of the temperature.

2. In the case of *dilute* solutions the relative depression increases in proportion to the concentration.

3. Defining molecular depression of the vapour pressure by the expression

$$\frac{p-p'}{p} \cdot \frac{m}{l},$$

in which m is the molecular weight and l the quantity of dissolved substance in, say, 100 grammes of the solvent, then the following statement is found to be true:—The molecular depression has a constant value for solutions of different substances if in the same solvent: it is, therefore, independent of the *quality* of the dissolved molecules.

The molecular depression, as here defined, is simply the depression obtained with a solution containing one gramme molecule of the solute in 100 grammes of the solvent.

4. The relative depression is equal to the ratio of the number of molecules of the solute to the total number of the molecules of the solute together with those of the solvent; or, in the form of an equation,

$$\frac{p-p'}{p} = \frac{n}{N+n},$$

in which n is the number of molecules of the solute and N of the solvent.

These results were obtained experimentally. But the last equation may be deduced theoretically from the laws of osmotic pressure, and thus the variations of vapour pressure serve to confirm van't Hoff's theory of solutions.

BOILING POINTS AND FREEZING POINTS OF SOLUTIONS.—Since the vapour pressure of a liquid is diminished when it contains a substance in solution, it follows that the boiling point of a solution is higher, and the freezing point lower, than that of the pure solvent. We should therefore expect these variations to give also a measure of the number of molecules in solution.

This, in fact, is found to be the case. The increase in the boiling point is proportional to the amount of the solute. If the observations are reduced to what may be looked upon as a normal solution, for example, a gramme molecule of the solute dissolved in 100 grammes of the solvent, we arrive at the molecular increase of boiling point. Representing this by B , we have

$$B = \frac{t - t_0}{w} M,$$

in which t_0 is the boiling point of the solvent, t that of the solution, w the number of grammes of the solute in 100 grammes of the solvent, and M the molecular weight of the solute. The right-hand side of this equation is simply the reduction of the observed rise to the normal solution. The value of the molecular increase of boiling point is found to vary with the solvent, but to be independent of the solute with some exceptions. Thus, using the same solvent, equimolecular solutions give the same increase of boiling point.

The same remarks apply to the depression of the freezing point. If the molecular depression is represented by F , we have

$$F = \frac{t_0 - t}{w} M,$$

in which the remaining letters have the same meaning as before, except that t_0 and t now refer to freezing points. By purely theoretical reasoning, based upon osmotic pressure, van't Hoff arrived at the equation

$$F = \frac{0.02T^2}{\lambda} M,$$

in which T is the freezing point of the solvent on the absolute scale and λ the latent heat of fusion of the solvent. The experimental and theoretical values for F are generally much the same. In the case of water, for instance, Raoult's observed molecular depression is 18.5 and the calculated value is 18.9. A similar formula holds for the rise of boiling point. We therefore find that van't Hoff's theory of solution is again experimentally confirmed.

BEHAVIOUR OF ELECTROLYTES.—Accurate observations upon osmotic pressure and vapour pressure are difficult to carry out. Determinations of freezing points, on the other hand, are comparatively easy; and, as all these phenomena are closely connected, results obtained for one hold for all. A large number of observations have been made by Raoult upon the depression of the freezing point, and later by Ponsot, Loomis, H. C. Jones and others. Now, although the various laws mentioned above hold for solutions which are non-electrolytes, it is found that abnormal results are at once obtained as soon as electrolytes are dealt with. Osmotic pressure and variations of vapour pressure, boiling point, and freezing point are all larger than would be expected, the effect increasing with the dilution. Electrolytes behave as if they consist of an abnormally large number of molecules. But these results are all readily explained if ionisation is assumed, and thus the observations of Raoult are to be regarded as confirmatory evidence in favour of the ionisation theory.

It must, however, be remembered that the phenomena that we have just been considering are not independent of one another, and that therefore evidence obtained from, say, osmotic pressure cannot be looked upon as additional to, and independent of, evidence in favour of ionisation obtained from freezing points. The chief foundation of the theory is based on what we have briefly described,

although there are other facts which we cannot enter into here. A critical examination of the whole theory would take us too far from our subject; we must therefore be content with saying that the belief in ionisation has spread to a wonderful extent on the continent and elsewhere, but it has met with a good deal of opposition in this country. The theory of Arrhenius only applies to very dilute solutions; concentrated solutions may be quite differently constituted, and therefore the theory is a very limited one. But the facts cannot be denied: the only question is the validity of the deductions. Ionisation is not necessarily the only way of accounting for these facts. For example, Poynting* has shown that Raoult's formula for vapour pressures, viz., $\frac{p-p'}{p} = \frac{n}{N+n}$, may be arrived at equally well by assuming that *association* takes place between solute and solvent instead of *dissociation* of the dissolved molecules. This hypothesis has been advocated by Armstrong.

More recent work by H. C. Jones, K. Ota and others has lead to the conclusion that both molecules and ions may combine with a varying number of molecules of the solvent, giving rise to what are conveniently termed "solvates" (corresponding to hydrates in aqueous solution). This effect is accentuated with increasing concentration, causing the solution to be virtually more concentrated than appears from the mere weights of the solvent and solute. Non-electrolytes appear to solvate but slightly.

A good deal of work has also been carried out on non-aqueous solutions, which seem at first sight to be irregular. For example, there are many cases in which the molecular conductivity decreases, instead of increasing, with increased dilution; and many solutions, which, according to molecular weight determinations, are not ionised, are good conductors.

* *Phil. Mag.* (5), Vol. 42, p. 289, 1896.

Thus, L. Kahlenberg* has carried out a number of determinations of the degree of ionisation of *aqueous solutions* by the boiling point and freezing point methods and also by the conductivity method, from low to very high concentrations. He found that there are solutions which are excellent conductors, but which do not show abnormal molecular weight of the dissolved substance. In some cases the molecular weight decreases with increase of concentration, finally becoming less than what it ought to be even on the assumption that ionisation is complete. It was found that, in many cases, there was not even a qualitative agreement between freezing points and boiling points of solutions on the one hand and their electrical conductivity on the other, as is claimed by the theory of Arrhenius.

It appears therefore that, in both aqueous and non-aqueous solutions, results have been obtained which are not in accordance with the ionisation theory in its simplest form and that account must also be taken of the solvent, more particularly if the solutions are not quite dilute.

Having considered the ionisation theory and some of the physical phenomena which are most closely connected with it, we are now in a position to pass on to the osmotic pressure theory of cells.

OSMOTIC PRESSURE THEORY OF CELLS. Electrolytic Solution Pressure.—When evaporation takes place from a liquid in a closed vessel, it continues until the pressure of the vapour so formed reaches a certain value, depending upon the temperature and upon the liquid. After this maximum value of the vapour pressure is reached, the condensation which then takes place is equal to the evaporation: although molecules may still be regarded as escaping from the liquid mass into the gaseous, an equal number are passing back from the vapour into the liquid, and so a state of equilibrium is established in which the

* *Journal of Physical Chemistry*, Vol. V., pp. 339-392, June, 1901.

vapour pressure is equal to and opposes the tendency of the liquid to pass into vapour. In the same way, the osmotic pressure of a saturated solution which is in contact with some of the undissolved solid substance may be looked upon as a measure of the "solution pressure" of the substance, or of its tendency to pass into solution.

In order to account for the E.M.F., or the difference of potential, between a metal and any electrolyte in which it is immersed, Nernst introduced the idea of "electrolytic solution pressure" of the metals. This is analogous to vapour pressure, and indicates, or measures, the tendency of a metal to pass into free ions when placed in an electrolyte. These free ions are positively charged, and therefore also the electrolyte containing them. Since both kinds of electricity result simultaneously, the metal must be negatively electrified, and will attract the positive ions to it. What is called a "double layer" of electricities results at the surface of separation between the metal and electrolyte. As soon as the attraction of the metal for the positive ions is equal to the solution pressure, equilibrium is established, and no more ions pass into solution. If they did so, the electrostatic attraction would become greater than the solution pressure, and the reverse process would set in, viz., ions would pass back into the molecular state. Very few ions suffice to bring about this equilibrium, because the ionic charges are large.

In the case of a liquid containing no ions of the metal in question, the value of the E.M.F. depends only upon the solution pressure. But if ions of the metal are present, the solution pressure is opposed by the osmotic partial pressure of the cations, and the E.M.F. is smaller. Let P be the solution pressure, and p the osmotic partial pressure due to the metallic ions already present. Three cases are possible. First, $P > p$: metal ions are produced and the metal becomes negatively electrified; but since the osmotic pressure opposes the solution pressure the

number of ions, and therefore also the E.M.F. so produced, is smaller than it would be if no ions were initially present. Secondly, $P=p$: in this case the metal does not become charged, because no more metallic ions can be produced, and therefore no E.M.F. results. Thirdly, $P < p$: in this case cations are precipitated, as it were, upon the metal, to which they give up their positive charges until the electrification is sufficient to repel the remaining cations. Consequently the metal is positively electrified and the solution negatively, an E.M.F. being produced which is opposite in sign to that in the first case, where P is greater than p .

Let us now calculate the value of this E.M.F. The ions at the surface of the metal where the "double layer"

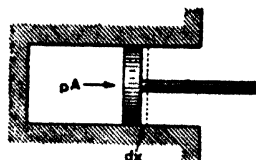


FIG. 30.—Work done by an Expanding Gas.

is formed may be looked upon as being under a pressure equal to the solution pressure, whereas any ions in solution are under a pressure equal to the osmotic partial pressure of those ions. If a current flows, due to the E.M.F., the ions pass from the pressure P to that of p , and in this change of pressure a certain amount of work must be done by the ions. Suppose gas under a pressure p to be confined in a cylinder, as indicated in Fig. 30, by a piston of area A . Then the total pressure outward upon the piston is pA . If the piston is allowed to move a very short distance, dx , outwards, so short that the pressure remains practically constant, the work done by the gas in so moving the piston is $pA dx$. But $A dx$ is the variation in volume, or dV , caused by the motion; and so the work done is equal

to the pressure multiplied by the change in volume. The total work done in varying from a volume v_1 to v_2 is given by the sum of such quantities, or by the integral

$$\int_{v_1}^{v_2} p dv.$$

Since in gases we have the relation $pv=RT$, the integral assumes the following value, viz. :—

$$\begin{aligned} RT \int_{v_1}^{v_2} \frac{dv}{v} \\ = RT \log \frac{v_2}{v_1} = RT \log \frac{p_1}{p_2}, \end{aligned}$$

where p_1, p_2 are the pressures corresponding with v_1, v_2 . In this expression the value of the constant R depends upon the basis on which we start: it is equal to the product of a volume into a pressure divided by the absolute temperature of the gas. If a given volume of gas be taken at a given temperature, the pressure is not defined by these two quantities, because it still depends upon the mass of gas with which we are dealing. By forcing more gas into the given volume the pressure would be changed, and the apparent value of the constant would also change. It is therefore necessary to deal with a definite mass. In our case the most convenient unit of mass is the gramme molecule. It will be remembered that a gramme molecule in the gaseous state occupies a volume of 22.38 litres at the normal pressure of 760 millimetres of mercury and at the normal absolute temperature of 273° . All our quantities are then defined, and the value of R , expressed as heat, is found on this basis to be 2 gramme-calories. With this value for R , the expressions given above represent the work done when a gramme molecule of a gas changes from the volume v_1 to v_2 or from the pressure p_1 to p_2 .

We may now continue the calculation of the E.M.F. When a current flows from the metal to the solution,

metallic ions pass from under a solution pressure P to the osmotic partial pressure p . If the electrolyte is a dilute salt-solution of the metal, supposed to be monovalent, it may be looked upon as completely ionised into equal numbers of two ions, and the value of p will then be equal to half the osmotic pressure, i.e., to the whole osmotic pressure which would result if no ionisation were to take place. Since the solute in a dilute solution obeys the gaseous laws, we may apply the results we have just obtained for a gas. It thus appears that when a gramme molecule of a monovalent metal passes voltaically into solution, work is done to the extent of $RT \log \frac{P}{p}$. But if E is the E.M.F. at the metal-liquid junction, and the work is wholly converted into electrical energy, this work is also equal to 96,500 E , because 96,500 coulombs of electricity are required to decompose one gramme molecule. Thus we have the relation

$$96,500 E = RT \log \frac{P}{p}.$$

The left hand side of this equation is expressed as work, and therefore R must also be expressed in that way. As already stated, it is equal to 2 gramme-calories, and thus to $2 \times 42 \times 10^6$ C.G.S. units of work. Remembering that a coulomb is $\frac{1}{10}$ of the C.G.S. unit, and that a volt is 10^8 C.G.S. units, we have for the value of the E.M.F. in volts

$$\begin{aligned} E &= \frac{2 \times 42 \times 10^6}{96,500 \times 10^{-1} \times 10^8} T \log \frac{P}{p} \\ &= 0.000087 T \log \frac{P}{p} \\ &= 0.0002 T \log_{10} \frac{P}{p}, \end{aligned}$$

the last value being obtained by converting the logarithms to the ordinary base of 10. If the temperature is 15°C , then $T = 288$, and

$$E = 0.0575 \log_{10} \frac{P}{p} \quad \text{at } 15^\circ\text{C}.$$

If the metal is not univalent we have the more general formula

$$E = \frac{0.0575}{n} \log_{10} \frac{P}{P'}$$

in which n is the valency.

Now consider the E.M.F. of a reversible cell, such as a Daniell. Here we have four contacts. The metal/metal and liquid/liquid contacts only give rise to small E.M.F.s which may in the first instance be neglected. At each of the metal/liquid junctions, however, we have metallic ions seeking to pass into solution; but this can only take place at one plate, deposition being necessary at the other. Consequently the E.M.F. takes the form

$$E = 0.0002T \left(\frac{1}{n} \log_{10} \frac{P}{p} - \frac{1}{n'} \log_{10} \frac{P'}{p'} \right),$$

in which the two component E.M.F.s oppose each other. The sign of either term in itself depends, of course, upon the solution pressure being greater or less than the osmotic pressure. In this expression the forces are supposed to be in equilibrium. It is the E.M.F. on open circuit, in which state the solution pressure diminished by the osmotic pressure of the metallic ions is equal to the electrostatic attraction of the double layer. But when the negative charge on the zinc is removed by closing the circuit, this equilibrium ceases. The positive charge of the double layer is then no longer bound, and consequently the solution pressure gives rise to more free ions; the zinc passes voltaically into solution and a continuous current is generated.

This theory of E.M.F. has been indirectly confirmed in many ways. For example, if the valencies n and n' are the same, and if the concentration of the ions is the same for both solutions, or $p = p'$, the formula simplifies to

$$E = \frac{0.0002}{n} T \log_{10} \frac{P}{P'}$$

In such a case the E.M.F. depends only upon the solution pressures, and, if the salts are assumed to be completely ionised, it does not change when the concentration of both solutions varies in the same way. That is to say, if the E.M.F. of a Daniell cell is 1.07 volts for given concentrations, it will remain at this value if the concentrations of the zinc sulphate and copper sulphate solutions are increased or decreased by the same amount. This result is easy to understand. An increase, for instance, in the concentration diminishes the E.M.F. at both plates; but, as these E.M.F.s oppose one another, the resultant E.M.F. remains constant (assuming equal ionisations). This is found to be approximately the case.

MEASUREMENT OF SINGLE E.M.F.s.—The existence of electrolytic solution pressure is purely hypothetical, for unfortunately we have no means of directly measuring it, or of proving that it does exist. Taking it for granted, however, that we have a statement of facts in the equation

$$E = \frac{0.0002}{n} T \log_{10} \frac{P}{p},$$

it should be possible to deduce the value of the solution pressure in many cases if we could measure single E.M.F.s, i.e., the E.M.F. due to a metal in contact with a liquid.

This E.M.F. must not be confused with the contact force between metals and liquids, which is a purely electrostatic effect and therefore unable to help us here. The determination of the Peltier effect at such a junction would give a measure of the E.M.F., but the value of such measurements is sometimes disputed. Fortunately, the work of Ostwald, Lippmann, Helmholtz, and others has rendered this possible in another way. One method of arriving at the required result is by means of a dropping mercury electrode. Suppose we have a mass of mercury which is allowed to run into an electrolyte in a fine stream. This stream is continuous near the jet, and may therefore be

arranged to form a connection between the electrolyte and the mercury in the reservoir. As the stream falls it breaks into globules. Now when such a stream starts, the mercury is positively electrified owing to the low value of its solution pressure. But as the flow continues the difference in potential diminishes. In the words of Helmholtz,* “. . . when a quantity of mercury, otherwise insulated, makes contact with an electrolyte by flowing rapidly through an orifice, the mercury and the electrolyte cannot be at different potentials. For if the potentials were different, *e.g.*, if the mercury were positive, each falling drop would present an electrical double layer at its surface, thus removing positive electricity from the mercury, and would gradually reduce the positive potential until it became equal to that of the liquid.” Thus the measurement of the single E.M.F. between mercury and a solution becomes comparatively easy. Usually the E.M.F. between two stationary mercury electrodes in the same electrolyte is zero, because the two potential differences involved are equal and opposite. But if one of these potential differences is removed by using a dropping mercury electrode, then the E.M.F. between the moving and the stationary mercury will be simply that between mercury and the solution.

The mode of action of a dropping mercury electrode may be shown by the simple arrangement given in Fig. 31. A burette serves as the mercury reservoir, and is supported about a centimetre above the surface of dilute sulphuric acid contained in a beaker, which also holds some mercury. Connection is made between the latter and a galvanometer *G* by a wire passing down a piece of glass tubing which is attached to the side of the beaker and dips into the mercury, thus protecting the wire from the acid. A second wire passes from the galvanometer down the bore of the burette, making contact with the mercury which it

* *Zeitschrift für Physikalische Chemie*, Vol. I., p. 584, 1887.

contains. Upon opening the tap, so that the mercury flows in a rapid stream, a deflection of the galvanometer will be observed.

Another method of measuring single E.M.F.s depend upon surface tension.

As the result of such measurements, it has been found that the E.M.F. between mercury and mercurous chloride in normal potassium chloride solution is 0.56 volt

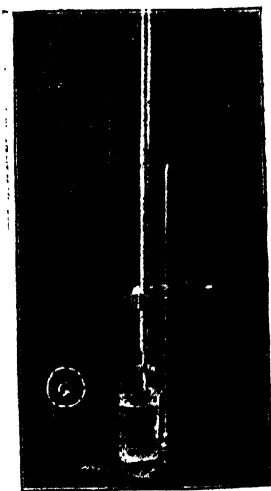


FIG. 31.—Dropping Mercury Electrode.

Knowing this, it is a simple matter to deduce other values on the assumption that the E.M.F. of a cell is the algebraic sum of two such potential differences. For example, if both plates tend to send cations into solution, they oppose each other, and we have

$$E = E_1 - E_2$$

as the resultant E.M.F. Supposing the E.M.F. of the cell, zinc/normal zinc sulphate solution/mercurous chloride

in normal potassium chloride solution/mercury, to be 1.08 volts, then, since ions tend to pass out of solution in the case of mercury, we have

$$1.08 = E_1 + 0.56,$$

$$E_1 = 0.52,$$

and therefore the value of the E.M.F. between zinc and normal zinc sulphate solution is 0.52 volt.

It should be noted that this value is larger than that resulting from the measurements of the Peltier effect by Bouty.*

CALCULATION OF ELECTROLYTIC SOLUTION PRESSURE.—We now have the means of calculating the values of the various electrolytic solution pressures. We have at a temperature of 15°C. the relation

$$E = \frac{0.0575}{n} \log_{10} \frac{P}{p},$$

or

$$\log_{10} P = \frac{nE}{0.0575} + \log_{10} p.$$

In the case of zinc, $n=2$; and if the solution is normal zinc sulphate, $E=0.52$. Also, if we suppose the sulphate to be completely ionised, then the osmotic pressure p due to a gramme molecule in a litre of solution will be 22.38 atmospheres.

Substituting these values, we find $P = 2.7 \times 10^{10}$ atmospheres.

The solution pressures of other metals may be calculated in the same way after deducing the values of corresponding single E.M.F.s.

The following examples, mostly due to Neumann, will give an idea of the results obtained, which vary somewhat according to the data on which they are based:—

Magnesium	1.15×10^{10} atmospheres	Lead	1.1×10^{-3} atmospheres
Zinc.....	2.7×10^{10}	Copper ...	4.8×10^{-20}
Iron.....	1.2×10^4	Palladium.	1.5×10^{-20}

* *Journal de Physique*, 1st Series, Vol. 8, p. 229, 1879; and Vol. 9, p. 366, 1880.

These figures will at once strike the reader as somewhat strange, most of them being enormously large or extremely small. It must, however, be remembered that such figures really only represent the striving of the molecules to pass into the ionic state, and the pressures here given are the osmotic pressures which it is necessary that the metallic ions already in solution should exert in order that no ionisation, and consequently no electrification, should take place. It should also be borne in mind that no such pressure has been directly or indirectly observed. All we can say is that if electrolytic solution pressure exists, and if it acts in the way here described, then the magnitude of the pressure must be of the order given above.

From our preliminary discussion of solution pressure, it will be inferred that those metals with the high pressures are negatively electrified, and those with low pressures are positive to solutions of their salts. Between these two extremes metals may be found which are not electrified at all if the concentration of the solution is suitable.

Having found the values of solution pressures, we are now in a position to calculate the E.M.F. of any reversible cell. But such calculations can in no way confirm the values we have already found for the solution pressures, because the latter are based upon the experimental determination of such E.M.F.s. It is simply a case of reasoning round in a circle, and therefore such calculations become of no further interest.

EFFECT OF VARYING THE NEGATIVE ION.—It will be noticed that the formula arrived at for the value of a single E.M.F. is quite independent of the negative ion: it only depends upon the osmotic pressure of those positive ions which are of the same metal as that which is immersed in the solution, and upon the electrolytic solution pressure of the metal. Thus we should expect the E.M.F. of zinc in zinc sulphate solution to be the

same as that of zinc in zinc chloride, provided the degree of ionisation is the same in both cases. This deduction has been verified by Neumann, who carried out measurements upon a large number of salts. Unfortunately these were mostly salts of organic acids, which are well known to produce no effect upon the E.M.F. Very decided changes, however, are often observed in passing from one halogen salt to another, and this fact led Bancroft* to the conclusion that, although a single E.M.F. is independent of the concentration when ions of the metal are not in solution, and also generally independent of the positive ion in such a case, yet it depends upon the negative ion and upon the solvent. He concluded further that in aqueous solutions the E.M.F. is the sum of two terms, one due to the electrode and the other to the negative ion. For most metals and most electrolytes the term due to the negative ion has the same arithmetical value and the same sign; but in the case of mercury the sign is opposite although the value is the same. A. E. Taylor† arrived at the conclusion that a single E.M.F. is not a function of the negative ion; he looks upon mercury and copper as exceptions, the effect in these two cases being probably due to the formation of complex salts.

COMPARISON OF THE HELMHOLTZ AND NERNST EQUATIONS.—Difficulties arise in the application of both these formulæ, although they are perfectly general from the theoretical point of view. In the case of the Helmholtz equation, it is only necessary to know the heat of a certain reaction and a temperature coefficient in order to arrive at a result. But the determination of the former may be difficult, and the actual reaction may be uncertain. When, for example, a cell is generating a current for some time the E.M.F. falls, apart from any

* *Physical Review*, Vol. 3, p. 250, 1896.

† *Journal of Physical Chemistry*, Vol. 1, p. 1, 1896.

polarisation effects. The reaction may still be the same chemically, though under altered conditions, and therefore different thermally; or it may be somewhat modified chemically. But these changes are such that we cannot well trace them and determine their thermal equivalents.

The equation of Nernst, on the other hand, is based on no chemical reaction, but rather on physical changes. Variation of E.M.F. with varying concentration is readily followed by referring to such an equation, whereas a change in the heat of reaction is not easily detected. Nevertheless, osmotic pressures may often be so small as to be indefinite, in which case the Nernst formula gives no precise result. It may, however, be said to give a more detailed insight, in some respects, into the working of a cell. The Helmholtz formula applies to a cell as a whole, for no voltaic chemical reaction can take place with a truly *single* contact, though we may perhaps consider each individual reaction as representing an E.M.F.

The preceding remarks will be rendered clearer by the consideration of a few examples. Let us first turn to the Helmholtz equation, and apply it to the simple cell $\text{Cu}/\text{H}_2\text{SO}_4/\text{Zn}$. The chemical part of the E.M.F. is readily calculated from the difference of the heats of formation of zinc sulphate and sulphuric acid, because zinc sulphate is formed and a corresponding amount of sulphuric acid is decomposed. We have, in fact,

$$[\text{Zn}, \text{O}_2, \text{SO}_2, \text{Aq}] - [\text{H}_2, \text{O}_2, \text{SO}_2, \text{Aq}] = 37,700 \text{ calories.}$$

The thermo-electric term, or temperature coefficient, must be found experimentally. Now, what will be the effect of replacing the sulphuric acid by a solution of zinc sulphate? If we suppose the current still to be due to the formation of zinc sulphate, we have the E.M.F. given by

$$[\text{Zn}, \text{SO}_4] - [\text{Zn}, \text{SO}_4],$$

because the sulphate is both formed and decomposed.

But this expression is zero. We may go a step further and replace the zinc sulphate by a solution of potassium sulphate. The chemical part of the E.M.F. would then, on the same supposition, be given by

$$[\text{Zn}, \text{SO}_4] - [\text{K}_2, \text{SO}_4] = -89,800 \text{ calories,}$$

(from Thomsen's data).

Thus by these changes, supposing such reactions to take place, the chemical part of the E.M.F. is first reduced to zero and then to a large *negative* value. Apart from the impossibility of the last reaction, which is so highly endothermic, it is found experimentally that the E.M.F. of the cell $\text{Cu}/\text{K}_2\text{SO}_4/\text{Zn}$ is 1.061 volts, the zinc being the electro-positive plate; further, the E.M.F. of such a cell is practically the same as when the electrolyte contains cations of the positive plate, as in the cell $\text{Cu}/\text{Zn SO}_4/\text{Zn}$ (Taylor, *l.c.*). The results also change but slightly if other salts are used. We must therefore conclude that the assumed reactions in the case of salt solutions are incorrect, and that, whatever the reaction may be, it must be of a general nature, not varying with the salt employed as the electrolyte.

Again, the E.M.F. is found experimentally to vary with the negative plate. For example, the E.M.F. of the reversible cell $\text{Ag}/\text{Ag NO}_3/\text{Pb}(\text{NO}_3)_2/\text{Pb}$ is 0.932 volt; but if any metal between silver and lead in the voltaic series is substituted for either of these metals, and the corresponding reversible cell is formed, the E.M.F. will be diminished. Thus, if copper is substituted for lead, we have the cell $\text{Ag}/\text{Ag NO}_3/\text{Cu}(\text{NO}_3)_2/\text{Cu}$, and the E.M.F. is reduced to 0.458 volt. How does the Helmholtz law account for this change? Part of it may be due to a change in the thermo-electric term, but the greater part must, owing to its magnitude, be due to the chemical term. As already shown in the case of the Daniell cell, the latter term is given by the difference of the heats of

formation of the two salts. For these two cells we have the chemical E.M.F. given by

$$[\text{Pb}, (\text{NO}_3)_2] - 2[\text{Ag}, \text{NO}_3],$$

and

$$[\text{Cu}, (\text{NO}_3)_2] - 2[\text{Ag}, \text{NO}_3]$$

respectively. Thus both the metals enter into the calculation, and the E.M.F. should consequently vary if there is a change in either of them, which is found to be the case. The above expressions may almost be looked upon as denoting a striving of both the plates after the negative ion.

But when we pass on to the single cell $\text{Cu}/\text{H}_2\text{SO}_4/\text{Zn}$, we find that only the positive plate enters into the thermo-chemical calculations, and the thermo-electric term is the only part of the Helmholtz equation which is affected by a change in the negative plate. This is unfortunately insufficient to account for the observed phenomena.

Passing again to the cell $\text{Cu}/\text{K}_2\text{SO}_4/\text{Zn}$, let us assume that the E.M.F. is due to oxidation of the zinc by the water. This reaction is independent of any particular salt, and therefore a change of the salt would not cause any change in the E.M.F., which is in accordance with experiment. Now, can the negative plate be supposed also to affect the E.M.F.? It certainly may do so if we suppose the plate to be to some extent oxidised. The oxidation will often be only extremely slight, but when it is remembered that the currents that can be generated by such cells are very minute, it will be allowed that the oxidation of the negative plate may be sufficient to act as a depolariser under normal conditions. We should then have oxidation of the positive and reduction of the negative; and, if the whole takes place voltaically, the chemical part of the E.M.F. of such a cell as $\text{Cu}/\text{Zn SO}_4/\text{Zn}$ is given by

$$\begin{aligned} & [\text{Zn}, (\text{OH})_2] - [\text{Cu}, (\text{OH})_2] \\ &= [\text{Zn}, \text{O}, \text{H}_2\text{O}] - [\text{Cu}, \text{O}, \text{H}_2\text{O}] \\ &= 82,680 - 37,520 \\ &= 45,160 \text{ calories} \\ &= 0.98 \text{ volt.} \end{aligned}$$

The observed value is 1.06 volts; but, as the calculated value does not include the thermo-electric term, the agreement may in reality be much closer. This way of regarding these cells thus permits the influence of the negative plate to appear as demanded by experiment, and in that respect is satisfactory, but further confirmation is necessary.

Unfortunately the E.M.F. of a cell which polarises rapidly is not easily determined. If the method of measurement selected necessitates the generation of current by the cell, then polarisation is at once introduced and causes the E.M.F. to appear lower than it really is. If, on the other hand, the generation of current is avoided by the use of an electrometer, we then become uncertain what E.M.F. we are really measuring: dissolved gases, for example, may exert a considerable influence, although not really the cause of the E.M.F. we desire to measure. It is, therefore, not a simple matter to decide these and many other theoretical points by an appeal to experiment.

Let us now look at the same cells in the light of the Nernst theory. In all cases we have to do with the electrolytic solution pressure of *both* the plates, and therefore a change in either plate must cause an alteration in the E.M.F. In a reversible cell, such as $\text{Cu}/\text{CuSO}_4/\text{ZnSO}_4/\text{Zn}$, everything is quite definite. We have the solution pressures of copper and of zinc opposed by the osmotic partial pressures of the copper and zinc ions in the electrolytes, as required by the formula

$$E = \frac{0.0002}{2} T \left(\log_{10} \frac{P}{p} - \log_{10} \frac{P'}{p'} \right),$$

neglecting any disturbance due to the junction of the two solutions.

But when a metal is placed in a solution containing no ions of that metal, the solution pressure is opposed by no osmotic pressure, and the single E.M.F. should be infinite in value. This is not, however, the case and therefore it may be concluded that a certain number

of ions always pass into solution, but we cannot say off-hand what the number should be, and consequently the E.M.F. of such a cell as $\text{Cu}/\text{ZnSO}_4/\text{Zn}$ appears to be rather indefinite. In this case there is no definite osmotic pressure of the copper ions, though the zinc ions exert a pressure which can be determined by suitable measurements as already explained. The same difficulty would be expected in the cell $\text{Cu}/\text{K}_2\text{SO}_4/\text{Zn}$. The latter may, however, be considered from the following point of view, as suggested by Bancroft.*

We have seen that the E.M.F. of a reversible cell is independent of the concentration, provided the ionisation is always complete. Now, instead of diluting the salts in the cell $\text{Cu}/\text{CuSO}_4/\text{ZnSO}_4/\text{Zn}$ with water, let us use K_2SO_4 for this purpose. According to the theory, the effect on the copper and zinc ions will be precisely the same, and we shall eventually obtain the cell $\text{Cu}/\text{K}_2\text{SO}_4/\text{Zn}$, which thus appears as a limiting case of the reversible cell $\text{Cu}/\text{CuSO}_4/\text{ZnSO}_4/\text{Zn}$, and should therefore have the same E.M.F. This view is to some extent supported by experiment.

In the above discussion it is assumed that no E.M.F. exists at the junctions of the solutions. As will be seen in the next chapter this assumption cannot always be made, but the E.M.F. is generally small.

A further difficulty arises when the solution pressure of a metal is very small, as for example in the case of copper and mercury. According to the hypothesis of Nernst, when mercury comes into contact with a solution of one of its salts, mercury ions are precipitated upon it, and it thus becomes positively electrified. This has been confirmed experimentally by W. Palmaer.† But if such a solution as potassium sulphate is used in place of a salt

* *Physical Review*, Vol. 3, p. 250, 1836.

† *Zeitschrift für Physikalische Chemie*, Vol. 28, pp. 257-279, 1899, and *Zeitschrift für Elektrochemie*, Vol. 7, pp. 237-239, 1900.

of mercury, no mercury ions are initially present, and therefore no such precipitation can take place. Nevertheless the mercury is found by experiment to be still positively electrified. This is generally explained by saying that, as soon as the solution touches the mercury, a little of it passes into solution, most probably as hydroxide, and the ions are then reprecipitated if their osmotic pressure is greater than the solution pressure of the metal. The amount of oxide necessary to effect the electrification would be very minute, but the explanation does not appear altogether satisfactory.

It has always been considered that the amount of metal which is dissolved in giving rise to an E.M.F. is too small to be determined by chemical means. Recently, however R. A. Lehfeldt* has shown that, in the case of zinc at least, the amount dissolved would be some centigrammes per square centimetre immersed. This point has been dealt with further in a later publication.†

THE ELECTRON THEORY.—Since the beginning of the present century great progress has been made in the Electron Theory of electricity, a theory which is intimately bound up with the name of Sir J. J. Thomson. According to this theory, the movement of electricity depends upon small corpuscles, far smaller than atoms, each associated with a definite negative charge. These may be looked upon virtually as atoms of electricity, and are termed electrons. There are both positive and negative electrons, but it is the negative electron which appears to be most readily affected; in fact, our acquaintance with the positive electron is comparatively small. It is assumed that the normal unelectric atom has, associated with it, an equal number of positive and negative electrons. If such an atom parts

* Paper read before the Brit. Assoc., 1899. *Phil. Mag.*, Vol. 48, pp. 430-433, 1899.

† *Phil. Mag.*, Vol. 1, pp. 377-403, 1901.

with a negative electron the atom becomes positively electrified owing to the resulting excess of positive electricity; on the other hand, if it receives a negative electron, there results an excess of negative electricity, and the atom then becomes negatively electrified.

The electron theory does not add materially to our knowledge of primary cells, but it gives us a simple way of looking at some of the phenomena. For example, when a piece of zinc is placed in contact with a piece of copper, negative electrons pass from the zinc to the copper, and so the copper becomes negative to the zinc. Thus contact force arises. This process continues until the P.D., tending to reverse this process, reaches a sufficiently high value to stop it. The potential varies with the metals that are taken, because some metals part with their electrons more easily than others.

In metallic conduction the electrons are looked upon as moving from atom to atom. Here, however, the theory presents difficulties. Kamerlingh Onnes has shown that at the temperature of liquid helium (i.e., nearly at absolute zero) the specific resistance of some metals is less than one hundred thousand millionth part of that at 0°C. Sir J. J. Thomson * has pointed out that such a phenomenon cannot be satisfactorily explained by an abnormal increase in the number of electrons or by variation in their mean free path, and that consequently the electron theory becomes untenable. He suggests an explanation on the theory that the atoms of some substances contain electrical doublets, or pairs of equal and opposite electrical charges at a small distance apart, and that the effect of an applied E.M.F. is to form polarised chains of atoms, after the manner of Grothius. Thus we may also explain the recently-discovered fact that a metal conductor cannot carry more than a certain limiting current—its saturation

* *Proceedings, Physical Society of London*, Vol. XXVII., p. 527.

current, where Ohm's law fails. This stage is reached when nearly all the atoms are orientated.

Passing from contact force and metallic conduction we come to the cell itself. Here we have an electrolyte in addition to the metals. In a solution where the molecules are not ionised each molecule is neutral, because the number of positive and negative electrons are equivalent. But when a molecule is ionised, the ions separate, the positive ion losing one or more negative electrons (depending on its valency) to the negative ion. Electrolytic solution pressure may be regarded as the tendency of a metal to send ions into solution and at the same time to give up negative electrons. Thus, when zinc is immersed in a solution of one of its salts, zinc ions tend to pass into solution, but in doing so the atoms must give up some negative electrons. They cannot give these up to the zinc ions already in solution because they would then become neutral—that is, they would become zinc molecules and would be deposited. Thus the electrons are left behind in the metal and the zinc becomes negatively electrified.

Taking copper as the other plate, the positive ions here tend to deposit, and in doing so they must extract negative electrons from the copper to render themselves neutral. Consequently the copper becomes positively charged. The metal that loses electrons most easily becomes charged positively.

CHAPTER VI.

NON-CHEMICAL CELLS AND THERMOPILES.

Concentration Cells, p. 119.—E.M.F. due to contact of Electrolytes, p. 120.—Liquid Cells, p. 122.—Becquerel's Cell, p. 123.—Thermo-Couples, p. 124.—Thermo-Electric Power, p. 126.—Practical Difficulties in Thermopiles, p. 128.—Gülcher's Thermopile, p. 129.

CONCENTRATION CELLS.—Suppose that, in a single cell, we have both plates of the same metal, and both standing in a solution of the salt of that metal, but the solution about one plate more concentrated than about the other. Such a cell, known as a concentration cell, has an E.M.F. and will produce a current; but this E.M.F. cannot be due to chemical action, because the passage of a current necessarily causes a definite amount of the positive plate to be dissolved and an equal weight of the same metal from the same salt to be deposited. The chemical actions are therefore equal and opposite, except for such a small difference as may be due to the difference in concentration, and therefore they cancel. Consequently the cell is not a truly voltaic one, and the E.M.F. must be due to energy other than chemical.

The application of the Nernst theory to this case affords an explanation. Let P be the electrolytic solution pressure of the metal, and p, p' , the osmotic partial pressures of the metal ions in the dilute and concentrated solutions respectively. The single E.M.F. due to the metal and dilute solution is, of course, greater than that due to the other plate in the concentrated solution, and therefore the

former must be regarded as electro-positive, the current in the cell flowing from the dilute to the concentrated solution. Consequently, neglecting any E.M.F. at the junction of the solutions, the E.M.F. of the cell is given by

$$E = \frac{0.0002}{n} T \left(\log_{10} \frac{P}{p} - \log_{10} \frac{P}{p'} \right) \\ = \frac{0.0002}{n} T \log_{10} \frac{p'}{p}.$$

From this it is seen that the E.M.F. is due simply to the difference in concentration. At a temperature of 15°C .

we have
$$E = \frac{0.0575}{n} \log_{10} \frac{p'}{p}.$$

Thus in the cell, silver $\frac{N}{100}$ silver nitrate solution $\frac{N}{10}$ silver nitrate solution/silver, the E.M.F. is given by

$$E = \frac{0.0575}{1} \log_{10} \frac{100}{10} \\ = 0.0575 \text{ volt,}$$

if we assume the ionisation to be complete in both solutions.

E.M.F. DUE TO CONTACT OF ELECTROLYTES.—We have so far neglected any E.M.F. at the contact of solutions, without however proving that we have any right to do so. Suppose we have a dilute solution and a concentrated one of the same salt in contact with each other, the ions being monovalent. In general, the velocities of the two ions will not be the same. Let u be that of the cation and v that of the anion. When a sufficient number of coulombs (viz., 96,500) passes to decompose one gramme molecule of the electrolyte, then $\frac{u}{u+v}$ and $\frac{v}{u+v}$ represent the proportions of this quantity carried by the cations and

anions respectively. If the current in the cell flows from the dilute to the concentrated solution, $\frac{u}{u+v}$ gramme atoms of the cation move with the current for every gramme molecule of the electrolyte decomposed, and pass from the dilute to the concentrated solution. At the same time $\frac{v}{u+v}$ gramme atoms of the anion are transferred in the opposite direction, as indicated in Fig. 31. Let p, p' , be the osmotic partial pressures of the ions in the dilute and concentrated solutions respectively. These pressures are, of course, the same for those anions and cations

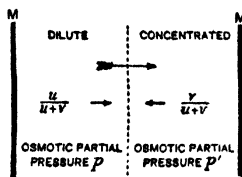


FIG. 31.

which are associated together in either solution. It therefore follows that the $\frac{v}{u+v}$ gramme atoms of the anion pass from a pressure p' to the lower pressure p , whereas the $\frac{u}{u+v}$ gramme atoms of the cation move from the pressure p to the higher pressure p' . Consequently, as we saw on page 102, the anions are capable of doing work to the extent of

$$\frac{v}{u+v} RT \log \frac{p'}{p}.$$

On the other hand, work must be done upon the cations to the extent of

$$\frac{u}{u+v} RT \log \frac{p'}{p}.$$

The energy that is available for doing external work is the

difference of these two expressions, and the E.M.F. is therefore given by the equation

$$96,500 E = \frac{v-u}{u+v} RT \log \frac{p'}{p},$$

or
$$E = 0.0002 \frac{v-u}{u+v} T \log_{10} \frac{p'}{p}.$$

From this it is seen that the E.M.F. is zero under two conditions:—(1) If the osmotic partial pressure, or the concentration of the ions, is the same in both solutions; (2) if the migration velocities of the two ions are equal. The value of E is negative when $u > v$, indicating that the current under those conditions flows within the cell from the concentrated to the dilute solution. If the ions have different valencies, n, n' (n being that of the cathion) the formula becomes

$$E = 0.0002 \frac{v}{n'} \frac{u}{n} T \log_{10} \frac{p'}{p}.$$

For the case of different electrolytes in contact the expression is still more complicated.

Cells of this kind, in which the E.M.F. is due to the contact of two electrolytes, are generally termed **Liquid Cells**, although it would seem more reasonable to include them in the class of Concentration Cells.

We are now in a position to give a complete expression for the E.M.F. of a concentration cell, such as that described at the beginning of this chapter. The E.M.F. must be the algebraic sum of the E.M.F.s at the plates and at the electrolytic junction, and is therefore given by the equation

$$E = \frac{0.0002}{n} T \left(\log_{10} \frac{p'}{p} + \frac{v-u}{u+v} \log_{10} \frac{p'}{p} \right) \text{ volts,}$$

$$= \frac{0.0002}{n} \frac{2v}{u+v} T \log_{10} \frac{p'}{p} \text{ volts.}$$

This formula assumes the ionisation in the solutions to be complete. If this is not complete, but has a value i

(which is consequently less than unity), the equation for E becomes

$$E = \frac{0.0002}{n} \frac{2iv}{u+v} T \log_{10} \frac{p'}{p} \text{ volts.}$$

Nernst has verified the truth of this formula. For example, in the cell, silver $\left/ \frac{N}{100} \right.$ silver nitrate solution $\left/ \frac{N}{10} \right.$ silver nitrate solution/silver, the values of the quantities involved are $n=1$, $u=52$, $v=58$, $i=0.935$, $\frac{p'}{p}=10$.

Thus at 18°C .

$$E = 0.0002 \times 2 \times 0.935 \times \frac{58}{52+58} \times 291.$$

$$= 0.0574 \text{ volt.}$$

The observed value was 0.055 volt.

BECQUEREL'S CELL.—The only liquid cell of interest is that known as Becquerel's cell. This consists of an acid

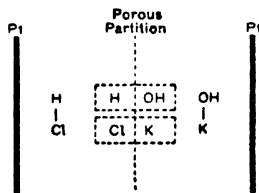
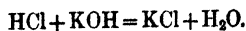


FIG. 32.—Reactions in Becquerel's Cell.

and an alkali, for example, hydrochloric acid and caustic potash solution, separated by a porous pot, a sheet of platinum dipping into each solution. Of course, where the acid and alkali meet in the porous division they interact, according to the equation



But such a reaction is not capable of giving electrical energy. As indicated in Fig. 32, there is no separation of ions in the sense required by voltaic action or electrolysis.

Nevertheless this cell has a considerable E.M.F., about 0.7 volt, although it is only capable of generating a small current. The origin of the E.M.F. has sometimes been supposed to be thermo-electric, the source of heat being due to the neutralisation of the acid by the alkali at the electrolytic junction. The E.M.F. is, however, too large to be so explained.

Referring to our discussion of liquid cells, it is seen that at least part of the E.M.F. in Becquerel's cell is due to the unequal migration velocities of the ions. But this will only account for part of the E.M.F. The remainder is probably due to the presence of atmospheric oxygen upon the platinum plates.

Berthelot* states, on experimental evidence, that the E.M.F. is equal to the sum of the E.M.F.s due to the junctions of the salt with the acid and base respectively. In other words, he considers the cell indicated in Fig. 32 to have a layer of KCl between the HCl and the KOH.

In the cells which we have just considered, the E.M.F. is not due to chemical action. Chemical changes do, of course, take place on account of electrolysis, but these must be looked upon as the effect, not as the cause. When chemical action is absent, the corresponding term of the Helmholtz equation vanishes, and it then reduces to $E = T \frac{dE}{dT}$; or the E.M.F. is wholly due to Peltier effects, and is proportional to the absolute temperature.

THERMO-COUPLES.—In accordance with the observations of Volta, no current flows in a closed metallic circuit of which all parts are at the same temperature. There is a contact E.M.F. at each junction, but these E.M.F.s are in equilibrium. Suppose we have two metals, say copper and iron. The E.M.F. Cu/Fe is equal and opposite to the

* *Comptes Rendus*, Vol. CXXXVI, 1903; *Science Abstracts*, Vol. VII A, No. 325 (1904).

E.M.F. Fe/Cu at the same temperature, and no current is produced. But if one of these junctions is heated, the equilibrium is disturbed, and there is a resultant E.M.F. This E.M.F., in some cases, increases continuously as the difference in temperature of the two junctions is increased; but generally the E.M.F. is observed to rise to a maximum as the temperature is increased, after which it diminishes as the temperature is still further increased, finally becoming zero, and then changing its sign. This phenomenon is known as *inversion*. After the temperature of inversion has been reached, the E.M.F. increases continuously, no higher or second temperature of inversion being as a rule reached. Representing the E.M.F. by the ordinates of

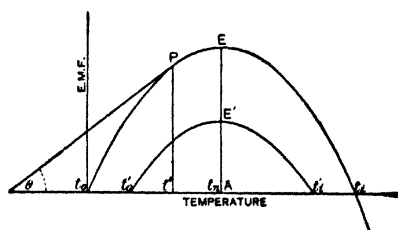


FIG. 33.—Curves of Thermo-Electric E.M.F.

a curve, and temperature-differences by abscissæ (the temperature of the cold junction being maintained constant), this curve is found to be an hyperbola, or approximately a parabola having the maximum ordinate as axis. Such a curve is shown in Fig. 33.

Here the temperature of the cold junction is t_0 . Upon heating the other junction, the E.M.F. rises gradually until it reaches the maximum denoted by AE, when the hot junction is at a temperature t_1 . It then falls gradually until it becomes zero at a temperature t_2 , the latter being as far removed from t_0 as t_1 is removed from t_0 . At a higher temperature the E.M.F. reverses. The temperature

t_n is called the *neutral* temperature of the two metals, and t_i the temperature of inversion. The curve $t'_n E t'_i$ shows the result obtained when the cold junction is kept at a higher temperature t'_n . The neutral temperature remains the same, the maximum E.M.F. now being reduced to AE' , but the temperature of inversion is changed from t_i to t'_i . The neutral temperature is always the mean between the temperature of the cold junction and that of inversion, and is therefore most easily found by observing the latter.

The thermo-electric properties of metals are most conveniently represented by reference to what are termed **thermo-electric powers**. The thermo-electric power of a pair of metals is given by the variation of the E.M.F. of the couple with temperature. It is therefore dE/dt , or the tangent of the angle of inclination of the tangent to the curve just considered. Thus, at the temperature t'' the corresponding tangent in Fig. 33 is at P, and dE/dt is given by the value of $\tan \theta$, in terms of the scales used for the co-ordinates. This value varies with the temperature, and therefore thermo-electric power is indefinite unless the temperature is stated. At the neutral temperature, for example, it becomes zero.

Thermo-electric powers are found to follow an additive law. If $(dE/dt)_{AB}$ indicates the thermo-electric power of the two metals, A, B, then we may write

$$(dE/dt)_{BC} = (dE/dt)_{AC} - (dE/dt)_{AB}.$$

In other words, the thermo-electric power of the couple BC is equal to the difference of the thermo-electric powers of C and B with regard to A. It is therefore only necessary to determine the thermo-electric power of metals with reference to some standard metal in order to be able to calculate the thermo-electric power of any couple among those metals. Lead is generally taken as the standard metal.

The curves showing the variation of thermo-electric power with temperature are generally straight lines, variously inclined to the axis, as shown in Fig. 34, in which the lines AA and BB may be supposed to represent the variation of thermo-electric power of the metals A and B with temperature. Thus at t_1 the value for A is t_1A_1 , while for B it is t_1B_1 , so that the thermo-electric power of the couple AB at t_1 is A_1B_1 . At t_2 it is A_2B_2 . Where the curves cross, the thermo-electric power becomes zero at the temperature t_n , which is the neutral temperature; the point C is called the *neutral point*.

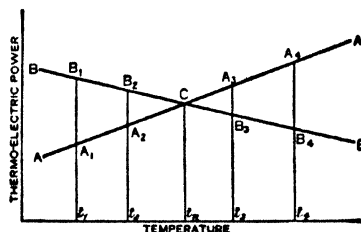


FIG. 34.—Thermo-Electric Powers.

Since the E.M.F. for the temperature limits t_1, t_2 , is given by the integral $\int_{t_1}^{t_2} \frac{dE}{dt} dt$, it follows that the area $A_1A_2B_2B_1$ represents the E.M.F. of the couple AB when the junctions are at the temperatures t_1, t_2 . When the hot junction reaches the temperature t_n , the E.M.F. is given by the area A_1CB_1 . As the temperature of the hot junction is still further raised to, say, t_3 , dE/dt becomes negative, and then A_3CB_3 has to be subtracted from A_1CB_1 to give the E.M.F., which is therefore diminished. When the hot junction reaches the temperature t_4 , such that A_4CB_4 is equal to A_1CB_1 , the resultant area, and therefore the E.M.F., is zero, and t_4 is the temperature of inversion.

PRACTICAL DIFFICULTIES IN THERMOPILES.—In the practical application of thermo-couples many difficulties are encountered. The E.M.F. of a single couple is always small. For example, that of a bismuth-antimony couple is about 0.000117 volt per degree centigrade, that of a copper-iron couple is about 0.000016 volt. Consequently a large number of couples must be connected up in series in order to obtain an E.M.F. of any practical value. Thus if 100 bismuth-antimony couples be in series and the junctions be maintained with a temperature-difference of 100°C. between them, as indicated in Fig. 35, the E.M.F. is only 1.17 volts.

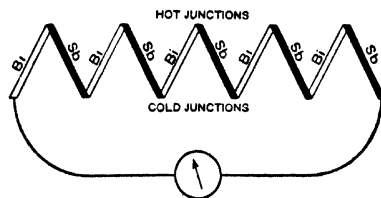


FIG. 35.

In the transformation of heat into electrical energy the efficiency of a thermo-couple is limited, for the heat which is absorbed at the hot junction is not all capable of transformation. The restriction mentioned on page 43 must be applied, and thus the efficiency cannot exceed $\frac{T_1 - T_2}{T_1}$, in which T_1 is the temperature of the hot junction on the absolute scale and T_2 that of the cold junction.

The question of efficiency in this case, however, is not a serious one; but, unfortunately, the practical conditions are conflicting and introduce considerable difficulties. For example, an electrical generator should have as low an internal resistance as possible; in other words, the metals should be good electrical conductors. But for the economical

maintenance of a high difference of temperature between the junctions, the conductors should be as far as possible insulators of heat. Good conductors of electricity, however, are found to be also good conductors of heat, and therefore the one condition can only be complied with at the expense of the other. If the conductors are made of small section, or long, so as to allow ready radiation, then the disadvantage of high internal resistance is also introduced.

On account of these various difficulties the actual efficiency of a thermopile is low. The all-round efficiency when it is generating a variable or small current is particularly low, because the heat energy is expended at much the same rate whether the pile is on open circuit or generating its maximum current. It is in fact equivalent to a galvanic cell having an enormous amount of local action.

It is also found that the deterioration of a thermopile is often comparatively rapid, causing complete breakdown in from three to five years. This is due no doubt to the continual expansion and contraction, and is apparently less marked if the thermopile is kept continually running.

GÜLCHER'S THERMOPILE.—This thermopile, supplied in three sizes in England by J. J. Griffin & Sons, is illustrated in Fig. 35A. It consists of two series of thermoelectric elements heated by two series of small Bunsen burners.

The tubes of the latter are seen at A. The heat of each flame is applied in a small hole of which there are two series, B, corresponding to the burners. These holes are fitted with small projecting tubes (not shown in the figure) which protect the upper parts of the elements C from unnecessary heating. The elements do not extend below the tops of the burners, but are supported on the base by sheet metal radiators, D, and are also kept in contact with

each other by means of screws which bear against the uprights E, E. Gas and air are supplied at F.

The makers give the following particulars:—

Number of elements	25	...	50	...	66
E.M.F.—Volts	1½	...	3	...	4
Current (when the external is equal to the internal resistance)—amperes	3	...	3	...	3
Internal resistance—ohms	0.25	...	0.50	...	0.65
Approximate consumption of gas per hour—Cubic feet...	2.6	...	4.9	...	6.4
Price	£6 7s. 6d.	...	£12	...	£14 5s.

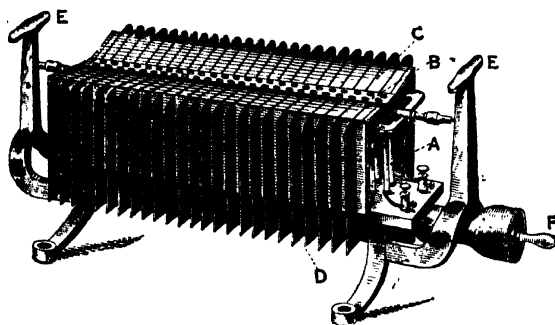


Fig. 35A.—Gulcher's Thermopile.

Notwithstanding the convenience of a thermopile of this kind, the high price permits the battery to hold its own without difficulty.

Various types, such as Clammond's thermopile and Cox's thermopile (which was described in the first edition of this work), have made their appearance from time to time, but have never secured any marked success.

CHAPTER VII.

TESTING CELLS.

Measurement of E.M.F., p. 131.—Measurement of Polarisation, p. 133.—Measurement of Depolarisation, p. 134.—Measurement of Internal Resistance, p. 134.—Measurement of Current, p. 138.—Testing Batteries of Low Current Capacity, p. 123.—Testing Batteries of High Current Capacity, p. 144. Dry Cells, p. 147

Before passing on to a description of the more prominent primary batteries now in use, it will be well to discuss briefly the various measurements which are made in testing a cell, so that the results accompanying the descriptions of cells in a later part of this volume may be more readily understood.

There are five chief electrical quantities which require to be measured—viz, (1) E.M.F., (2) Polarisation, (3) Depolarisation, (4) Internal resistance, (5) Current.

1. E.M.F.—It is, of course, important that a cell should have a high E.M.F., because the higher the E.M.F. the fewer the number of cells required to give any desired pressure. Moreover, other things being equal, the electrical energy is generated more cheaply. The amount of material consumed in a cell depends only upon the *quantity* of electricity generated, and is independent of the E.M.F. Consequently, if two cells, both consuming materials of the same value, have E.M.F.s of one volt and two volts respectively, the latter will generate a watt-hour more cheaply than the former—viz., at half the cost. Unfortunately, cells seldom have an E.M.F. higher than two

volts; frequently it is much lower. The cause of this was referred to on page 52.

The E.M.F. of a cell does not generally require to be measured to a high degree of accuracy, and therefore the simplest and most usual method of measurement is by means of a direct-reading voltmeter whose resistance is high compared with that of the cell. When such is the case, the potential difference at the terminals of the voltmeter is practically the same as the E.M.F. of the cell. To ensure a true result, the resistance must also be so large that the E.M.F. is not appreciably diminished by polarisation when the voltmeter is in circuit.

A convenient form of voltmeter for laboratory measurements consists of a reflecting galvanometer whose deflections are proportional to the current—for example, a d'Arsonval galvanometer with curved pole pieces. Such an instrument should be permanently fitted up with a large series resistance, so that one volt gives a deflection of a convenient number of divisions, say 100. The resistance may be in the form of a plug resistance box, so that the sensibility may be readily altered by changing the plugs.

The well-known compensation method of Poggendorff is an excellent one for measuring an E.M.F. by comparison with that of a standard cell; but it is somewhat troublesome, and is capable of giving results which are far more accurate than is generally required for this class of work. A simpler and less accurate method, but one which is sufficiently accurate for the purpose, is that which depends upon comparison by means of a condenser. For this comparison a reflecting galvanometer is required and a condenser, of say, one-third of a microfarad capacity and having good insulation. The condenser is first charged by connecting to the standard cell, and immediately discharged through the galvanometer. It is then charged by the cell whose E.M.F. is to be determined, and again discharged through the galvanometer. In both cases a

deflection of the galvanometer needle is observed which is proportional to the charging E.M.F., and thus the two E.M.F.s are in the ratio of the two deflections. The E.M.F. of the standard cell being known, that of the other cell is at once deducible.

2. POLARISATION.—Polarisation is the most serious of the electrical defects found in voltaic cells, though the seriousness of the defect in any given cell depends upon the use for which it is intended. Thus, the polarisation in a Leclanché cell is much greater than in a Grove cell; but it does not follow that the former is useless: since the Leclanché (of equal size) is used on circuits where smaller currents are required, the comparatively large amount of polarisation is of little importance. In carrying out tests it therefore becomes necessary to decide what strength of current the cell will, under ordinary circumstances, be required to furnish, and then to measure the polarisation for that particular current. Since polarisation increases until the rate of depolarisation is equal to that of polarisation, it will be preferable to maintain this current until a somewhat steady state has been reached, or for as long a time as it is likely to be required under working conditions.

A simpler and more definite method is to close the cell through a resistance of, say, 5 ohms for one hour, and then to observe the E.M.F. In this way cells are readily compared, but the currents generated are not, of course, the same, the current being greater where the polarisation is less; and therefore a cell which polarises but slightly is put to a more severe test than one in which that defect is more serious.

The accurate measurement of polarisation is a matter of some difficulty, but approximate results may be obtained with ease. The E.M.F. is first of all observed before the cell is placed on circuit. The cell is then closed through

a resistance which may be adjusted until the desired current is flowing. When this current has been maintained as long as desired, the circuit is broken, after which the E.M.F. is immediately observed. The difference between this E.M.F. and that initially observed gives the value of the polarisation under these particular conditions. The difficulty encountered is that the E.M.F. often recovers from polarisation very rapidly, especially so just after opening the circuit. It is for this reason that the observation should be made *immediately* upon breaking the circuit. This is most readily effected by using the condenser method.

3. DEPOLARISATION.—In order to observe the recovery from polarisation, it is only necessary to take further measurements of the polarised E.M.F. which has been observed as above. These measurements should be taken at short intervals after breaking the circuit. The observations may then be plotted as a curve upon sectional paper, the E.M.F. being represented by ordinates and the time from breaking the circuit by abscissæ.

4. INTERNAL RESISTANCE.—It is generally desirable that the internal resistance of a voltaic cell should be low, for when that is the case the potential difference on closed circuit is more nearly equal to the E.M.F., and more of the electrical energy is utilised in the external circuit.

The value of the internal resistance is obtained by observing the value of the potential difference upon closing the cell through a known resistance. On page 14 we saw that the following relation holds good, viz. :—

$$\frac{E - V}{V} = \frac{r}{R},$$

$$r = \frac{E - V}{V} R,$$

in which r and R are the internal and external resistances respectively, E is the E.M.F. of the cell, and V is the potential difference. Consequently, if E , V and R are known, then r is deducible.

This, however, assumes that E is unchanged by the current that is generated. In reality, polarisation is certain to set in; and, although the value of r will satisfy the above equation, it will not be the true value of the internal resistance, because the E.M.F. will have fallen.

In order to eliminate polarisation, the circuit should be closed only just long enough to obtain an observation. Fig. 36 shows a method which may be used. It is the

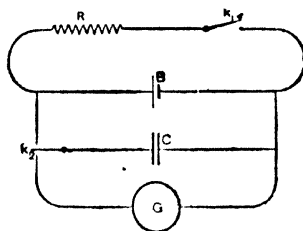


FIG. 36.—Measurement of Internal Resistance.

external resistance through which the cell B is closed upon depressing the key k_1 : this key should make good contact, so that R is practically the only resistance in circuit. If the key k_2 is raised the cell charges the condenser C , but if k_2 is depressed the condenser discharges through the galvanometer G . In making a test a deflection corresponding to the E.M.F. is first observed. The key k_2 is then raised, k_1 is closed, and k_2 is immediately depressed: a deflection on the galvanometer is observed, and is a measure of the potential difference.

A rough idea of the value of the internal resistance may be obtained by connecting up a suitable voltmeter to the cell, noting the E.M.F., and then closing the cell through

a known resistance with the voltmeter still attached. The deflection will be seen to fall. As soon as it is observed, the external circuit is broken and the value of the polarised E.M.F. is immediately noted. The difference between the two last readings will be approximately equal to $E - V$ in the formula.

Unfortunately, $E - V$ is generally small unless R is small. But if R is made small, the current is large and the polarisation is largely increased. This renders the difficulties greater. Since the internal resistance is directly proportional to $E - V$, it is readily seen that its determination is very liable to be inaccurate unless suitable precautions are taken.

On page 37 a curve was reproduced showing the apparent variation of internal resistance with the current generated by a cell. In an investigation of that kind it is necessary that polarisation should be very thoroughly eliminated. Consequently, the various operations in the condenser method—viz., closing the circuit, charging the condenser, discharging through the galvanometer, and finally opening the circuit—should all be accomplished by some mechanical device, so that they are repeated at regular intervals of time. In this way the disturbing influences of absorption by the condenser and of polarisation may be practically eliminated.

For this purpose Carhart used a pendulum consisting of a narrow frame pivoted at the top and carrying a heavy bob at the bottom. The details of the apparatus are best described in the observer's own words.* "The bob swings between two curved rails, concentric with the axis of suspension of the pendulum, and each rail supports two keys, which can be clamped on it in any desired position. A vertical lever on each key holds it closed on the lower contact; but when the pendulum sweeps over the rails it

* *Phys. Rev.*, Vol. II., p. 392, 1894-5. See also *The Electrician*, Vol. XXXV., May 3, 1895, p. 18.

throws these levers over and allows the spring keys to make contact on the upper point. The contacts are all platinum, and the base and pillars of the keys are hard rubber. When care is taken to adjust the contacts properly, and to keep them free from dust, their performance is in every way satisfactory."

Fig. 37 "shows the connections for the measurements in hand. Keys K_1 and K_4 are on one rail, while K_2 and K_3 are on the other. When the lever of K_1 is thrown forward, while that of K_4 is up, the battery circuit is closed through the resistance of R . When the lever K_2 is thrown over, while that of K_3 is up, the battery is charging

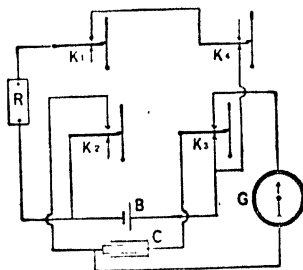


FIG. 37.

the condenser C ; but as soon as the lever K_3 is thrown over, the cell is disconnected from the condenser and the latter is instantly discharged through the galvanometer G . The pendulum swings from left to right on removing a detent. If all the levers are up, it closes the battery circuit on reaching K_1 , charges the condenser by throwing over lever K_2 , discharges it through the galvanometer by means of K_3 , and finally opens the battery circuit on passing K_4 . The key levers remain forward out of the way of the pendulum bar as it swings back to the detent. The keys can be set as close together as desired. The length of the pendulum is such that its period is a second.

Hence the time during which the battery circuit remains closed can be calculated. To get the deflection proportional to the total electromotive force of the cell, the levers K_1 and K_4 are both left down. The pendulum then charges and discharges the condenser, the circuit through R remaining open."

5. CURRENT.—It is, of course, often necessary in battery tests to measure the current generated, but the measurement of this quantity does not call for any detailed description in this volume. A galvanometer shunted by a resistance of known value, as described on a later page, will be found convenient for dealing with small currents. The larger currents are most suitably measured by some reliable form of ammeter, such as the Weston instrument. It is often desirable to put the ammeter in circuit only when a reading is required; but the additional resistance inserted in the external circuit by so doing may considerably change the value of the current. This difficulty is most readily obviated by having a resistance, equal to that of the ammeter, which is cut into the circuit when the ammeter is removed and is cut out when a reading is required, or by using an ammeter with a shunt.

TESTING CELLS OF LOW CURRENT CAPACITY.—

There is a large class of batteries, including Leclanché cells and dry cells, which is intended only for the supply of small or intermittent currents. They are used chiefly on bell and telephone circuits. Such cells of necessity differ considerably from those that are required to furnish heavier currents, and they should therefore be tested accordingly. In all cases the tests applied should depend upon the use for which the battery is intended.

As an example of a cell test, some curves (kindly furnished by Messrs. Siemens Bros. and Co.) relating to a small Obach dry cell are reproduced in Fig. 38. The cell

was closed through a resistance of 5 ohms for one hour. It will be noticed that the terminal P.D. fell from 1.47 to 1.305 volts during that time, giving rise to a corresponding fall in the current generated. The value of the internal resistance rose very slightly, as shown by the next lower curve. The initial value of the E.M.F. (judging from the curve of internal resistance) was about 1.56 volts. On breaking the circuit at

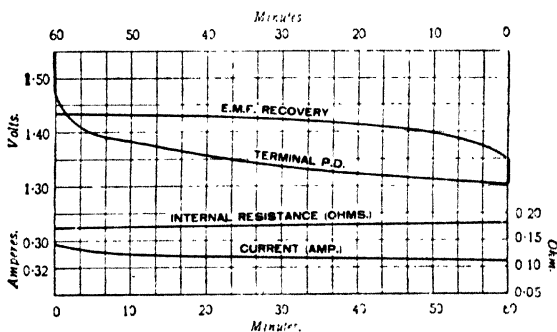


FIG 38.—Test of an Obach Dry Cell, size D (5 in. high overall \times 2 in. diam.), closed through a Resistance of 5 Ohms for One Hour.

the close of one hour the E.M.F. was 1.35 volts, showing that the polarisation amounted to 1.56—1.35, or 0.21 volt. The E.M.F. recovered rapidly from its polarised condition, so that it rose to 1.43 volts at the end of a second hour, as shown by the recovery curve, which must be followed in the reverse direction to the other curves.

Such a test gives valuable information as to depolarising qualities, but not much else. Its use is therefore somewhat limited. What is really required is a comparative life test, for the life of such cells is the quantity with which we are most concerned. Unfortunately, it is

impossible to determine the life of a cell of this kind under ordinary working conditions, because the time required would be far too long. Some method must therefore be adopted which will be to some extent equivalent. Intermittent-current tests, in which the cell is alternately generating current and resting at regular intervals, have been frequently employed. A bell has sometimes been used, the circuit being closed at intervals, in which case the number of hours the cell is able to ring the bell is looked upon as the measure of the life. But an electric bell is by no means a scientific measuring instrument. The length of time that a cell will cause ringing depends upon the resistance and adjustment of the bell. Consequently a bell is only suitable for making comparisons when cells can be worked intermittently upon the same bell and at the same time, the circuits being so arranged that when one cell is working another one is at rest. The reader should refer to Chapter X. in which various tests are described in connection with dry cells. It should also be noted that different tests do not necessarily give the same order of merit for a series of cells, for some cells will test better intermittently than continuously, and *vice versa*. It is often doubtful whether intermittent-current tests give any more information than those in which the current is continuous, and the latter have the advantage of greater simplicity and of giving a result in a shorter time. In a continuous-current test the cell is closed through a constant resistance, frequently of 10 ohms, and the time required for the current to fall to a certain value—for example, half its initial value—is regarded as a measure of the life. There is, however, an objection to taking half the initial value, because this figure is dependent upon the internal resistance as well as upon the E.M.F. Thus, if a cell gives at first a current of 140 milliamperes, its life will be finished when it falls to 70 milliamperes; but if one of the same cells

has a higher internal resistance, so that it gives initially only 120 milliamperes, its life will not be considered at an end until the current has fallen to 60 milliamperes. Consequently, a defect—viz., high internal resistance—gives the advantage of a lower current limit, and therefore the chance of a longer life. A low E.M.F. gives the same apparent advantage. The life is also likely to be longer because the cell is virtually closed on a higher resistance than the cell first mentioned. To overcome this defect to some extent, the Author prefers to take as a standard an ideal cell having no internal resistance and a definite E.M.F. Thus, a Leclanché cell should have an E.M.F. of 1.5 volts, and, if the internal resistance is nil, it should give 150 milliamperes when closed through 10 ohms. Its life will be terminated when the current falls to 75 milliamperes, and actual Leclanché cells may be compared by running them until the current falls to 75 milliamperes irrespective of the initial value of the current. This method has been employed by the Author in the tests described later in this volume. There still remains, however, the difficulty that a high internal resistance gives an advantage, because the cell is virtually on a circuit of higher resistance, and will therefore take longer to reach the lower current level. It would probably be preferable to make the *total* resistance (*i.e.*, inclusive of the internal resistance) equal to 10 ohms, if only the internal resistance remained a constant quantity when a current is being generated. The adjustment, however, of the external resistance to meet the variations of internal resistance during a life test would be troublesome. Without troubling to make the adjustment, the apparent advantage of high internal resistance may be eliminated to some extent by taking into consideration the number of ampere hours, or watt hours, furnished by the cell during its life.

At the end of a life test carried out in this manner the recovery of the E.M.F. may be observed for say

24 hours, after which the internal resistance should be measured and its value compared with that found at the beginning of the test. It should, however, be remarked that recuperation tests carried out at the end of a life test are not of much value for comparative purposes. It is preferable to make such tests upon new cells as described in connection with Fig. 38.

In cells of the kind now under consideration, which generally include as an electrolyte the aqueous solution of a salt, local action is very slight; in fact, it must be so for the cell to be of any value for intermittent work. Although it is unnecessary to make any efficiency tests, it is nevertheless well to look out for local action; also for unequal corrosion of the zinc, and for the various mechanical defects to which this class of cell is liable.

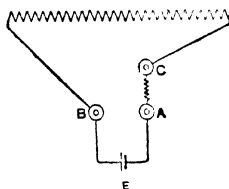


FIG. 39.—Arrangement of Circuits for Testing.

If a number of such cells are to be tested, it will be found convenient to have a d'Arsonval galvanometer arranged for directly indicating the E.M.F., or P.D., or current that a cell is generating. Suitable coils of 10 ohms each may be made in the form of spirals of No. 22 gauge platinoïd wire. Each coil is attached to insulators and the ends taken to terminals A, B (indicated in Fig. 39), which serve for connecting up the cell E and also for putting the galvanometer in circuit. Connection with the galvanometer should be made by means of brass plugs which fit into sockets in the terminals. Mercury cups may be employed for this purpose, but they are in many ways objectionable.

The galvanometer may be calibrated by means of a potentiometer and a standard cell, the series resistance being adjusted so that 1 volt gives a deflection of, say, 100 or 200 scale divisions. So long as the deflections follow a straight line law, they are then readily expressed in volts, the instrument being practically direct reading.

If the resistance is disconnected from B or C the galvanometer reading gives the E.M.F. of the cell: as soon as the external circuit is closed the reading indicates the potential difference. Also, since the external resistance is 10 ohms, the reading of the potential difference gives the current in milliamperes that the cell is generating. Sometimes, however, it may be necessary to employ an external resistance differing from 10 ohms, in which case the value of the current is not so simply indicated. It may then be desirable to introduce a third terminal C, and to place a small resistance of known value between A and C. The potential difference which will be set up between A and C when a current of 100 milliamperes is flowing is then calculated, and the resistance in series with the galvanometer is adjusted so that this potential difference will give a deflection of 100 or 200 divisions. When the galvanometer is connected to A and C it thus becomes a direct-reading ammeter, indicating milliamperes. In using a galvanometer shunted by a resistance in this way as an ammeter, it is, of course, necessary to remember that the resistance of the galvanometer circuit should be large compared with the resistance between A and C, otherwise the introduction of the galvanometer will cause a fall in the potential difference between A and C, and the deflection will indicate a smaller current than is actually flowing.

Fig. 40 shows part of a group of ten such circuits, which the Author has found very convenient in testing batteries of the Leclanché type. The plug connections and ammeter resistances are fitted in a box, behind which are

seen the remainder of the external resistances. The plugs are shown at I, I, from which flexible cord is connected to the galvanometer.

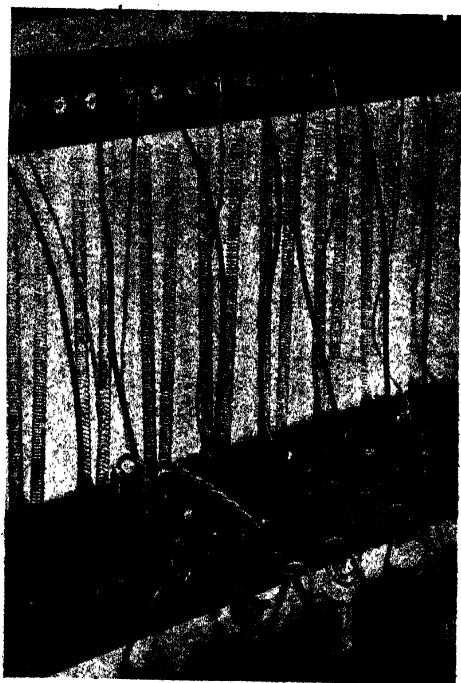


FIG. 40.—Apparatus for Testing Cells.

TESTING CELLS OF HIGH CURRENT CAPACITY.—

The great difference between this class of cell and that just considered is that cells of this class are generally intended to give a certain current continuously, and in testing any cell it is well to bear in mind what

current it is designed to generate. The circuits upon which batteries are placed are usually of more or less constant resistance, and in order that the work shall be efficiently performed a battery should be capable of giving a practically constant current within certain limits. In other words, when a cell is closed through a resistance, such as to permit the normal current of the cell to be generated, the polarisation must be but slight and the internal resistance fairly constant. A test should therefore be carried out by closing the cell through a suitable resistance and taking readings of the current at stated intervals. The current may remain reasonably steady for a number of hours, but finally it will fall rapidly, and the cell is then said to be exhausted. Such a cell may still be capable of generating a smaller current than the normal for some time, but for practical purposes its life must be considered at an end and the cell useless until re-charged. The value of the resistance selected for such a test must depend, of course, upon the purpose for which the cell is intended.

In carrying out a systematic test, two distinct sources of inefficiency must be investigated. The first of these is local action, the second is internal resistance. Supposing zinc to be the positive plate, we know that for every ampere hour furnished by a cell 1.21330 grammes of zinc should be dissolved. The amount dissolved is really always greater than this—sometimes very much greater—on account of local action. It is therefore generally necessary to take the weight of the plates of a cell before and after a life test, in order to see to what extent the loss of weight is greater than that required by the number of ampere hours furnished by the cell during the test. Since local action continues whether the cell is generating a current or is on open circuit, it follows that an efficiency test carried out in this way will give different results according to the conditions of the test. The conditions

should therefore be, as far as possible, similar to those under which the cell would be used in practice. For example, if in practice the cell would be left on open circuit with the plates standing in the electrolyte during considerable intervals, such intervals should be included in the efficiency test.

Local action is generally objectionable only because it shortens the useful life of a cell and thus causes inconvenience. In the case of primary batteries the question of cost is usually of less importance than that of convenience, such batteries being used for the supply of energy on a very small scale. If, however, primary batteries are ever used for power purposes, the question of local action will be an important one, as being one of the factors which directly affect the cost per unit.

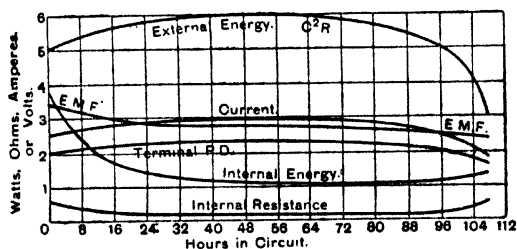


FIG. 41.—Test of Edison-Lalande Battery, four cells in series.

With regard to the second cause of inefficiency, it need scarcely be remarked that the internal resistance should be as low as possible. For a given cell the inefficiency increases with the current, and therefore some value of the current must be selected as normal. Apart from inefficiency, internal resistance is objectionable because it limits the potential difference available at the terminals of a cell.

The curves in Fig. 41 are a good example of the result obtained in testing this class of cell. The test was carried

out by A. E. Kennelly upon four Edison-Lalande cells coupled in series. It will be noticed that the current is remarkably steady, keeping between 2.5 and 3.0 amperes for about 95 hours. The fall in E.M.F. is only very slight, and is in a measure compensated by the fall in internal resistance. The efficiency, as regards internal resistance, is seen to increase considerably at the beginning of the test and to diminish somewhat at the end. This is shown by the curve for C^2R , which is the amount of electrical energy expended at any time in the external circuit. A corresponding curve is given for the energy dissipated in the internal circuit, which energy cannot, of course, be utilised.

It is always well to include a curve showing the watts in the external circuit. The current flowing may be large, but its practical utility will be small unless the watts in the external circuit form a large proportion of the whole. In other words, it should be possible to obtain a large current without making the external resistance unduly small, compared with the internal resistance. The external watts are, of course, proportional to the P.D., and the internal (or wasted) watts are proportional to the E.M.F. minus the P.D.

DRY CELLS.—Special considerations enter into the testing of dry cells, and therefore this part of the subject will be considered in detail in Chapter X.

CHAPTER VIII.

ONE-FLUID CELLS.

Classification of Cells, p. 149.—Smee Cell, p. 149.—Velvo Carbon Cell p. 150.—Bichromate Cell, p. 152.—Comparison of Depolarisers in Bichromate Cells, p. 157.—Chromic Acid, p. 157.—Potassium Permanganate, p. 158.—Advantage of Porous Pot, p. 159.—Two-fluid Bichromate Cells, p. 161.—Defects in Bichromate Cells, p. 161.—Partz Acid Gravity Cell, p. 163.—Benkö Cell, p. 164.—Special Electrolytes for Bichromate Cells, p. 172.—Lalande Cell, p. 173.—Edison-Lalande Cell, p. 176.—Walker-Wilkins Cell, p. 182.—Harrison Cell, p. 184.—Bellini's Cell, p. 190.—Silver Chloride Cell, p. 192.—Sulphate of Mercury Cell, p. 193.—Leclanché Cells, p. 193.—Porous Pot form of Cell, p. 195.—Agglomerate Block Cell, p. 200.—Central Zinc Cells, p. 207.—Sack Cells, p. 210.—Comparison of various types, p. 216.—Effect of Physical Quality of the Manganese Peroxide, p. 217.—Cells for Postal Work, p. 224.—Post Office Specifications, p. 225.—Details of Leclanché Cells, p. 231.—Special Exciting Salts, p. 232.—Amalgamated Aluminium, p. 234.

CLASSIFICATION OF CELLS.—In giving a description of primary batteries they will be divided into two classes, viz., (1) one-fluid and (2) two-fluid batteries. Of the former, dry batteries form such an important section that they will be considered separately; and for a similar reason standard cells will be classed by themselves.

Batteries are sometimes classified according to the work for which they are intended; but such a classification is not very satisfactory, because the work which a cell is capable of doing depends not only upon its construction but also upon its size.

Simple Cells.

THE SMEE CELL.—This cell is practically a "simple element," in which the difficulty of polarisation is more or less eliminated by employing the principle of "physical depolarisation," described in Chapter III. The cell consists

of a zinc positive, dilute sulphuric acid, and a negative of platinum or other suitable metal, so roughened that the deposited hydrogen does not adhere to it. This roughened surface is produced by means of platinising, *i.e.*, by electrolytically depositing a slight coating of platinum in a very finely divided state. Instead of a platinum plate, one of platinised silver or copper may be used, but if the latter is employed it should be varnished at the edges.* The platinising may be effected either by the application of an external E.M.F., or by making the plate to be platinised the negative in a voltaic cell, opposing it to a zinc rod in dilute sulphuric acid containing some platonic chloride, and short-circuiting the cell so formed.

The Smee cell is convenient on account of its simplicity, but it does not appear to have come into extended use, except perhaps by electro-chemists. This may be due to the low value of the E.M.F. which is stated to be 0.47 volt.

THE VELVO CARBON CELL.—The principle of Smee has been revived in recent years in the Velvo Carbon cell, in which the essential feature is the carbon negative. The surface of carbon in its usual state is unsuitable for rapidly disengaging the voltaically deposited hydrogen. This difficulty is overcome in the Velvo Carbon cell by a new process of manufacture. The carbons are formed from Lacombe arc light rods, 9mm. in diameter, with velvet seen cemented upon them and afterwards carbonised at a high temperature.† This gives a very large surface, from which the hydrogen is freely disengaged. A number of these rods are fixed in a frame, connection being made with a common terminal by means of a silver wire wedged into the carbon rods. The use of silver in this way appears to

* A. Smee, *Phil. Mag.*, 3rd Series., Vol. XVI., p. 315, 1840.

† *The Electrician*, Vol. XXXIII. p. 564, 1894.

give a connection of very low resistance, and one that is moreover unaffected by the acid electrolyte.

In Fig. 42 are shown the plates of a 180 ampere-hour Velvo Carbon cell leaning against the glass containing-vessel: one of the zinc plates has been removed so as to allow the "palisade" of carbons to be seen. The size of the zinc plates is 7in. by 9in.; the frame, which carries 13 carbons and also the two zinc plates, one on each side, is 7in. by 10 $\frac{1}{2}$ in.; and the glass vessel, which is capable of accommodating two "palisades" if desired, is 8in. by 4in. and 11in. high.



FIG. 42.—Velvo Carbon Cell.

The E.M.F., when the cell is freshly set up, using sulphuric acid of specific gravity 1.180, is 1.5 volts, but the effective E.M.F. is only about 0.8 volt, which corresponds with the thermo-chemical data of the reaction involved. The higher value is probably due to oxygen occluded in the carbon, which rapidly becomes exhausted when the cell is called upon to supply a current. If such a cell is short-circuited for some hours, the E.M.F., on breaking circuit, rises rapidly to 0.8 volt, after which it recovers very slowly.

In Fig. 43 is given a discharge-curve obtained by the Author upon short-circuiting a Velvo Carbon cell of the size referred to above through a Weston ammeter for eight hours. It will be noticed that the current is remarkably steady.

An objection to the cell is that when the plates are taken out of the acid to avoid local action on open circuit, crystals of zinc sulphate are liable to form in the porous carbon and to cause the velvet covering to flake off. The carbons should be kept in water when not in use. Another objection, and one which is shared by all "simple cells," is the evolution of hydrogen.

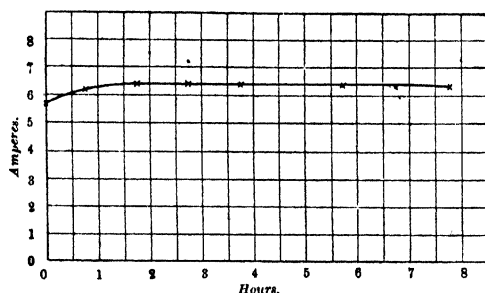


FIG. 43.—Discharge of Velvo Carbon Cell on Short Circuit.

Unfortunately, the Velvo Carbon cell appears to be no longer (Nov., 1901) upon the market, notwithstanding its very good qualities for a certain class of work.

Bichromate and Chromic Acid Cells.

THE BICHROMATE CELL.—This cell, which has been largely used for laboratory purposes, has plates of zinc and carbon, the electrolyte being a solution of sulphuric acid and either a bichromate or chromic acid. This acid, whether free or in the form of a bichromate, plays the part of a depolariser, the CrO_3 being reduced by the

polarising hydrogen to the lower oxide Cr_2O_3 , causing the well known change in colour from orange red to a dark blue. The Cr_2O_3 does not appear as such, being converted into sulphate by the excess of sulphuric acid. The E.M.F. is about 1.9 to 2 volts.

The electrolyte may be made up according to the following formula, which is given by Ayrton in "Practical Electricity" (4th edition):—

Potassium bichromate	1lb.	1lb. 2½ozs.	0.5 kilogramme
Concentrated sulphuric acid ...	2lbs.	1 pint	1 kilogramme
Water	12lbs.	11 pints	6 kilogrammes

Quantities expressed in pints and in kilogrammes have been added to the above, as it is frequently inconvenient to measure in lbs.

It is sometimes stated that the pulverised bichromate should first be added to the sulphuric acid, and the water then added to the resulting mixture. As good a result, however, is obtained if the bichromate is first dissolved in the water and the acid added to the resulting solution. The latter operation is also simpler, as hot water may be used for dissolving the bichromate, and the temperature reached on adding the acid to this solution, when cold, is not high; whereas the temperature may rise inconveniently if water is added to the concentrated acid. It is for this reason that, in diluting sulphuric acid, the acid should always be added to the water, and not the water to the acid.

When a cell charged according to the above formula fails, it is on account of exhaustion of the acid rather than of the bichromate. It may therefore be advisable to use more acid, say $2\frac{1}{4}$ lbs. instead of 2 lbs., as above stated.

In Fig. 44 is shown a bottle form of bichromate cell, which is convenient for experimental work where only

small cells are required. On account of local action, zincs should never be allowed to stand in cells having acid electrolytes when not in use. This precaution is particularly necessary in the case of bichromate cells, because the local action not only means waste of zinc, but also reduction of the depolariser by the liberated hydrogen, and thus a rapid deterioration of the cell. In the particular form of cell shown in Fig. 44, provision is made



FIG. 44.—Bottle Form of Bichromate Cell.

for raising the zinc out of the electrolyte when the cell is not in use. This is effected by attaching the zinc plate, which is placed between the two carbon plates, to a central rod which can be raised or lowered and clamped in any position.

For more extensive experimental work it is convenient to have a battery of, say, half a dozen cells coupled up in series, or with some arrangement for coupling in series or

parallel at will. Such a battery, made by Trouvé, of Paris, (and supplied in England by J. J. Griffin and Sons, London), is shown in Fig. 45. Each cell contains one zinc placed between two carbon plates of the same size, and all the plates can be raised or lowered by means of a winch running along the top. Similar batteries working on more or less the same principle are supplied by a number of makers.

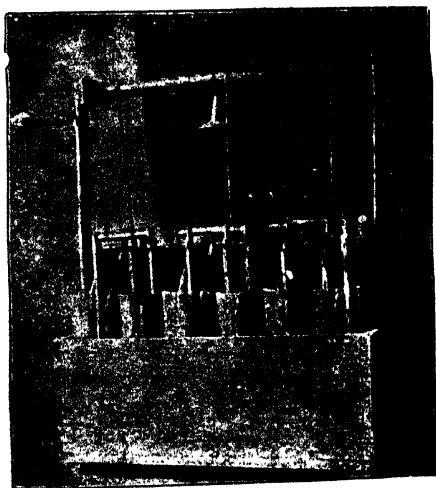


FIG. 45.—Trouvé Bichromate Battery.

If potassium bichromate is used in open batteries of this kind care should be taken not to allow the electrolyte to evaporate excessively, as crystals of chrome alum are liable to form at the bottom of the jars and are troublesome to remove.

Some discharge curves of bichromate cells are given in Fig. 46. The cell from which these were obtained had two carbon plates, one on each side of the zinc; the width of all the plates was 6in. and they were immersed to a

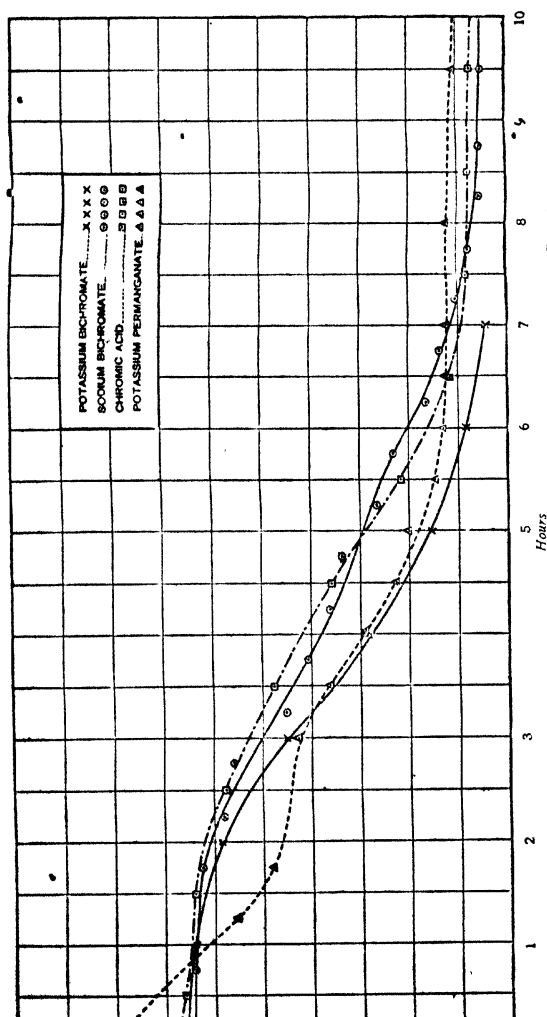


FIG. 46.—Discharge Curves of Bichromate Cells, showing Relative Values of Various Depolarisers.

depth of about 6½ in. The resistance of the external circuit was half an ohm. From these curves it is seen that the bichromate cell is capable of giving a heavy current for only a short time, after which the current falls off rapidly.

COMPARISON OF DEPOLARISERS. POTASSIUM AND SODIUM BICHROMATES.—The depolariser which is

generally used in bichromate cells is potassium bichromate, but in many respects other substances are preferable. The curves in Fig. 46 are the result of a rough comparison of depolarisers carried out by the Author. In each case, except that of potassium permanganate, which *does not* readily dissolve to the required extent, the quantity of depolariser in solution was taken so that the oxidising power was the same. It is seen that the discharge curve furnished by potassium bichromate is the shortest, the current falling to 0.4 ampere in six hours. A better result is obtained with sodium bichromate, the curve of which fell to 0.4 ampere in 7¾ hours. It appears, moreover, that the sodium salt does not give rise to alum crystals so readily as does the potassium salt, and, being deliquescent, it is much more easily dissolved. Since sodium bichromate crystallises with two molecules of water of crystallisation, whereas the potassium bichromate is anhydrous, the equivalent weights of the two salts are practically the same. The price is also much the same, and, therefore, the sodium salt is to be preferred.

CHROMIC ACID.—As the oxidising power of a bichromate is due to the chromic acid, the acid itself may be used as the depolariser in place of the salt. The curve in Fig. 46 relating to the use of the acid is seen, on the whole, to be slightly above that of sodium bichromate, the current falling to 0.4 ampere in 8½ hours. The lower part of the curve is superior to that of either of the bichromate salts, *e.g.*, it took over 12 hours for this particular cell to

fall below 0.3 ampere. (This point is not included in the diagram.) Chromic acid not only has the advantage of being as good a depolariser as sodium bichromate, or even better, but it has the further advantage that it dissolves almost instantly, giving a solution with a minimum of trouble and does not give rise to troublesome crystals on evaporation. Since the quantity of chromic acid required is only slightly above two-thirds that of potassium or sodium bichromate, in order to obtain a solution which is ready for immediate use it is only necessary to weigh out, say, 12 ozs. of chromic acid, pour 11 pints of water upon it, and then add one pint of concentrated sulphuric acid to the solution with constant stirring (*see* formulæ, p. 153). In small quantities, the price of chromic acid at present (1914) is 9½d. per lb. ; potassium bichromate is 6d. The latter is, therefore, about one-third cheaper, but as one-third less of chromic acid is required than of potassium bichromate, it follows that the cost is much the same for either depolariser. Since a reduction of 20 per cent. in the amount of chromic acid used does not appear to change the form of the discharge curve to any great extent, we may conclude that chromic acid is preferable to either of the bichromates.

POTASSIUM PERMANGANATE.—The fourth curve in Fig. 46 refers to potassium permanganate, of which only about 70 per cent. of the equivalent quantity was used on account of the difficulty experienced in making a more concentrated solution. It is noticeable that the E.M.F. is higher than with other depolarisers (it was found to be 2.1 volts), but the current falls rapidly at first, rendering this depolariser unsuitable for heavy currents. Nevertheless, complete exhaustion takes place more slowly than with the other depolarisers; the 0.4 ampere limit was reached only after 13½ hours with this particular cell, and the current did not fall below 0.3 ampere for 226 hours. The latter part of the discharge is, however, relatively unimportant.

It therefore appears that potassium permanganate is not a very satisfactory depolariser. Apart from the unsuitable form of the discharge-curve there is the further objection that the permanganate is troublesome to dissolve, and a heavy muddy deposit is formed on discharge.

We may therefore conclude that of the four depolarisers here discussed, chromic acid is the best for all practical purposes.

ADVANTAGE OF POROUS POT.—One of the advantages of the bichromate cell is that it is a one-fluid cell, and therefore simple. It is, however, sometimes used as a two-fluid cell by placing the zinc in a porous pot. If the latter contains some mercury the zinc keeps in a better state of amalgamation than is otherwise possible, and local action is thereby reduced.

In Fig. 47 are reproduced some curves of discharge which the author obtained from two-fluid bichromate cells. The cell used throughout these tests consisted of two carbon plates $3\frac{1}{2}$ in. wide, immersed to a depth of $5\frac{1}{2}$ in. between which was placed a zinc plate of the same width immersed to a depth of 4 in. The cell contained a total of about $1\frac{1}{2}$ pints of electrolyte. The external circuit had a resistance of $2\frac{1}{2}$ ohms.

The lowest curve in Fig. 47 is the discharge curve of the cell containing no porous pot, chromic acid solution (as described on p. 158) being the electrolyte. If the zinc is surrounded by a porous pot, *the electrolyte remaining precisely the same* (viz., chromic acid solution throughout), the discharge curve is seen to be very much improved. Thus the current falls to 0.6 ampere in $4\frac{1}{2}$ hours in the first case, but requires 11 hours to fall to the same value in the second case. Consequently, from the purely electrical point of view, a great advantage is gained by the introduction of a porous pot, *i.e.*, by keeping the electrolytic products at the two plates quite separate from each other.

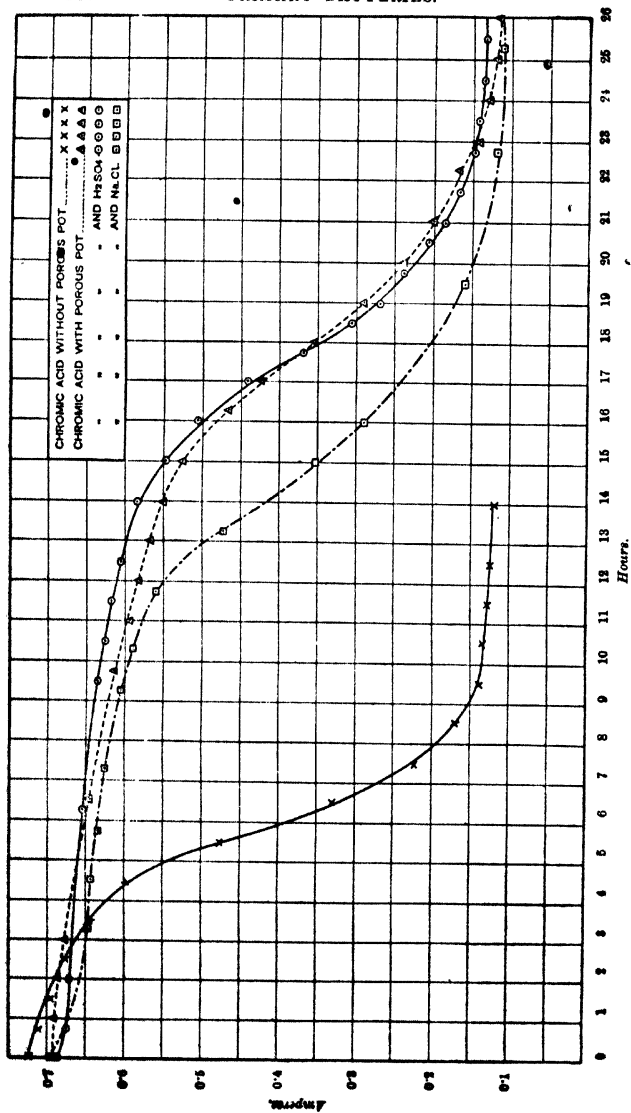


Fig. 47.—Discharge Curves of various kinds of Richmanite Cells.

TWO-FLUID BICHROMATE CELLS.—The remaining curves in Fig. 47 refer to true two-fluid bichromate cells. It is seen that they are all very similar to the curve obtained above with a porous pot. For example, that obtained by substituting dilute sulphuric acid (one volume of acid to ten of water) for the chromic acid solution in the porous pot, but not around the carbon, is very nearly the same as the curve for chromic acid. From this it appears that the presence of the depolariser in the neighbourhood of the zinc has no bad effect.

The remaining curve refers to the use of common salt (3oz. to a pint of water) in the porous pot surrounding the zinc. The discharge of another cell was observed in which zinc sulphate (6oz. to a pint of water) was used in the same way, but this curve has not been introduced into Fig. 47 because it so nearly coincides with the curve which refers to the porous pot containing chromic acid that it would only serve to confuse the diagram. The results obtained with common salt and zinc sulphate are of interest, because they show that the discharge does not suffer by the use of a neutral salt, the use of which is otherwise beneficial because it diminishes local action.

DEFECTS IN BICHROMATE CELLS.—There are three principal defects in the bichromate cell, viz.: (1) Rapid fall of current, (2) local action, (3) evaporation and consequent crystallisation. The last defect may be avoided by the use of a closed cell, such as the bottle form. These, however, are only made in small sizes, and it is therefore best to render evaporation harmless by avoiding the use of potassium bichromate. The first defect is remedied to a considerable extent, as has been shown, by introducing a porous pot, and local action is reduced to a minimum in the same way because the porous pot may contain sufficient mercury to maintain the zinc in a good state of amalgamation. This method is adopted in Fuller's cell,

the zinc in which is in the form of a lump attached to the end of an amalgamated copper rod. The local action between the zinc and the amalgamated copper is but slight; and as the mercury has only a short length of zinc to creep up, the amalgamation of the latter is well maintained. This method of mounting the zinc has the further advantage that no part of the zinc projects above the surface of the electrolyte, where, in general, local action is excessive.

In Fig. 48 is shown a similar kind of cell made by Messrs. Siemens. The zinc, however, is longer than that

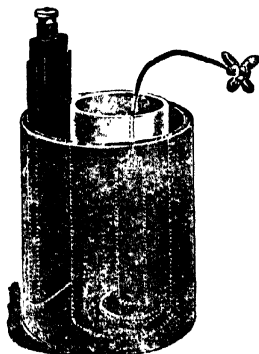


FIG. 48.—Bichromate Cell with Porous Pot.

just referred to. The porous pot should contain an ounce of mercury and may be charged with water or very dilute sulphuric acid, enough acid diffusing through the porous pot from the depolarising solution in the outer jar to sufficiently reduce the internal resistance. The Author prefers to use zinc sulphate for this purpose. The levels of the electrolytes in the two compartments should be about the same; and the porous pot when not in use should preferably be kept in water to prevent crystallisation in the pores and consequent disintegration.

PARTZ ACID GRAVITY CELL.—This cell, which is shown in Fig. 49, is ingeniously designed so that the diffusion of the acid depolariser from the carbon to the zinc is prevented by gravity. The carbon, whose effective area is increased by openings as shown, is placed at the bottom of the cell. It is connected to the positive terminal by a carbon rod, seen on the right hand side. A porous pot, which is coated with paraffin on the bottom and up the sides to a height of about two inches, rests upon the carbon plate. The object of the paraffin is to prevent diffusion of

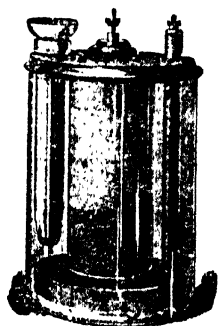


FIG. 49.—Partz Acid Gravity Cell.

the acid solution through the lower part of the porous pot which contains the zinc. The latter is suspended from the cover, and is long enough to reach to the top of the paraffin coating. To charge the cell, both compartments are filled with a solution of magnesium sulphate, or common salt. The depolariser is in the form of a "sulphochromic salt" in which sulphuric acid is united with chromic acid. The tube on the left, which is open at the top and tapers down to a small opening at the bottom near the carbon plate, is filled with this solid, and then inserted in position. A layer of depolarising solution thus forms over the surface

of the carbon by diffusion, and so remains if the cell is not handled. This cell gives an E.M.F. of 1.9 to 2 volts, and appears to have given satisfaction in America. It is stated that the Philadelphia Electrical Bureau used about 125 cells, of the Partz type for four years without a single failure, and at the end of that time the original zincs were still being used and were in good condition. A set of 62 cells that gave 1.34 volts and 2.3 amperes when first set up gave 1.20 volts and 1.5 amperes at the end of the four years.*

THE BENKO CELL.—One of the chief difficulties in using primary cells for heavy currents is that the depolarisation is not sufficiently good. Polarisation in itself would not be so bad if only it would remain constant, but it generally becomes greater and greater as time goes on during discharge. An Hungarian engineer, Stephan Benkö, eliminated this difficulty by removing the layer of electrolyte on the positive plate (electro-negative element) as fast as polarisation sets in, so that the E.M.F. remains constant for a given current.

The method adopted by Benkö is to use a carbon electrode sufficiently porous to allow the electrolyte to flow through it, thus continually providing a fresh supply to the surface that is tending to polarise. This will be understood by referring to the diagram, Fig. 50. Here the carbon is shown at C, and this is best described as a flattened cylinder open at both ends. The hard surface of this carbon, as received from the carbon makers, is removed by scratch-brushing so as to leave it easily porous. The carbon is then provided with a lead cap, L_1 , at the bottom, and a lead ring, L_2 , at the top, thus providing a vessel open only at the top. To obtain perfect contact between the carbon and the lead, the latter is put on under pressure by the simple expedient of holding the carbon in a suitable iron holder and dipping it

* *Western Electrician*, Vol. XXVI, p. 92, Feb. 10, 1893.

to a depth of 2 metres in a bath of molten lead. A lead shell, L_2 , of sheet lead 1 mm. to $1\frac{1}{2}$ mm. in thickness is then fitted round the carbon, leaving a small space between the carbon and the shell, and is jointed autogenously to the lead cap at the bottom and the lead ring at the top, so as to form a chamber all round the carbon. We thus have two chambers, one inside the carbon and one outside. The

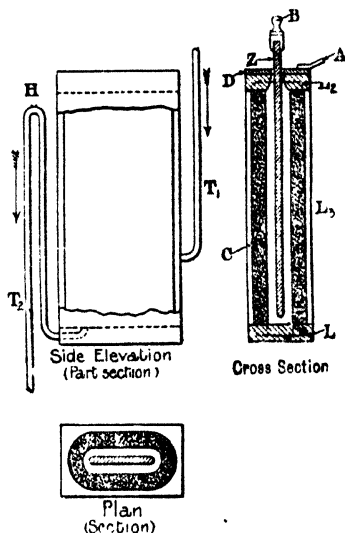


FIG. 50 — Diagram of Beekö Cell.

outer chamber is provided with a tube, T_1 ; and a second tube, T_2 , is fitted to the lead base and is carried through to the inner chamber. This latter tube is carried up and bent over, and there is a small hole, H , at the top of the bend. Finally a copper plate D corresponding with the lead ring is soldered on to the lead, and forms one terminal, A , of the cell. (In later designs this copper plate has been aban-

done, the terminal being jointed direct to the lead ring.) The zinc Z is inserted into the inner chamber, and carries the second terminal B. When in action the electrolyte is delivered by the lead tube T_1 into the outer chamber, whence it percolates through the carbon to the zinc; it then flows off through the lead tube T_2 , the form of which maintains the level constant within the carbon. As there is a hole at H, siphoning does not occur, though this may be made to take place in cells so constructed by closing the hole with a finger for a few minutes. This is often convenient when it is desired to empty the cell. It will be noticed that the current is carried away from the carbon at both top and bottom, and owing to this form of construction, and to the excellent contact between the carbon and the lead, very much heavier currents can be taken than is possible with the usual form of joint.

A working drawing of an actual cell is reproduced in Fig. 51, in which the lettering of Fig. 50 is retained as far as possible. It will be noticed that the space provided between the carbon and the lead shell is very small, only $\frac{1}{2}$ mm. The lead, however, gives somewhat under the pressure of the electrolyte, and for that reason it is supported by a wood casing (not shown). The zinc plate is carried in an ebonite frame, F. The tubes T_1 , T_2 are provided with unions and rubber washers, W_1 , W_2 , for coupling to other tubes as may be found necessary. (The tube T_2 is not shown carried up.) Larger cells are made by fitting two or more carbons into one shell.

In the case of a battery, the electrolyte is contained in a lead-lined tank, from which it flows (due to its own head) into a common supply pipe, from which each of the cells is supplied, the junctions being by ebonite unions and rubber washers, as already described. Similarly, the waste from each cell is carried into a common waste pipe, from which an inverted U pipe is taken to maintain the level in the cells.

Although the individual cells are not connected with each other metallically, they are connected by the electrolyte, and therefore local currents must flow. These, however, do not seem to be serious in a battery giving, say, 10 volts. With this arrangement the Author has found that, for a

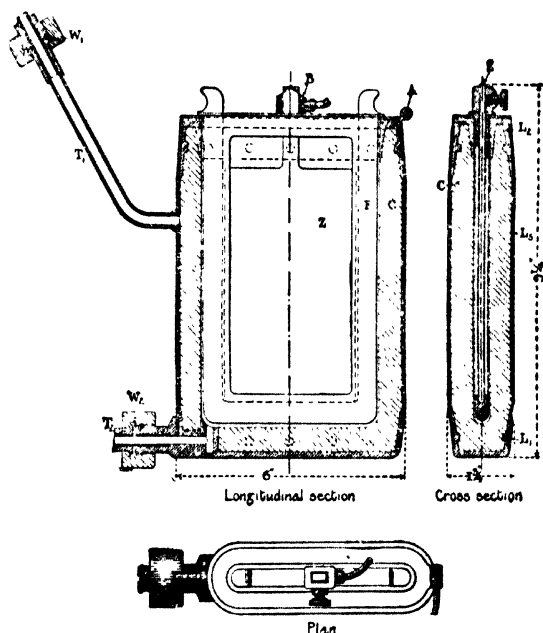


FIG. 51.—Single Benkö Cell (Standard Type).*

given flow of electrolyte, an extremely constant current can be maintained up to a certain limit. This limit depends largely, of course, upon the composition of the electrolyte. Various electrolytes may be used, and in the case of bichro-

mate solutions Benkö recommends the following formulæ, the equivalents being given also in English measure :

Water	1 litre.	35 fluid oz.	} L. solution.
Sodium bichromate	60 grammes.	2.1 oz.	
Sulphuric acid (concentrated), sp. gr. 1.84	120 c.c.	4.2 fluid oz.	
Water	1 litre.	35 fluid oz.	} P. solution.
Sodium bichromate	100 grammes	3.5 oz.	
Sulphuric acid (concentrated), sp. gr. 1.84	150 c.c.	5.25 fluid oz.	

Potassium bichromate should not be used, as it tends to deposit double sulphate crystals when decomposed, and these block up the pores of the carbon. The E.M.F. with these solutions is 2.0 volts, rising sometimes to 2.05 volts.

The maximum currents obtainable continuously with these solutions in terms of the area of the zinc (taking both sides into the measurement) may be taken as 6 amperes per square decimetre (56 amperes per square foot) for solution L and 10 amperes per square decimetre (93 amperes per square foot), the rate of flow being high. It is not desirable to allow the voltage to fall below 1.5 volts per cell, and when the flow is restricted to $\frac{1}{2}$ litre per cell per hour the permissible current falls to a lower value than these figures. Local action is less than in the ordinary types of acid cell on standing because the amount of electrolyte in the cell at any one time is comparatively small.

In order to show the capabilities of the Benkö and ordinary bichromate cells (without porous pot), the curves in Figs. 52 and 53, obtained by the Author,* are given. Fig. 52 shows the record taken by a recording ammeter of the discharge of a Benkö cell along with plotted curves of terminal pressure and terminal watts. The weight of the cell, including casing, electrolyte and zinc, was about 10 lb.,

* "The Benkö Primary Battery and Its Applications," by W. R. Cooper, *Journal, Inst. El. Eng.*, Vol. XLVI., p. 741, 1911.

and of the size shown in Fig. 51. It is seen that a remarkably constant current of over 12 amperes was taken from the cell for six hours, and the current was then increased to over 17 amperes for about two hours. The latter part of the discharge took a little time to become steady, due, no doubt, to the additional heating of the cell.

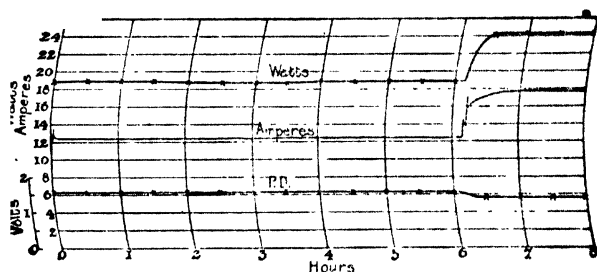


FIG. 52.—Discharge Curves of Benkő Cell, Solution "L."

The bichromate cell used for comparison held 3 pints of the same electrolyte, and had one zinc plate and two carbons; all three plates were $6\frac{1}{4}$ in. wide, and were immersed to a depth of $7\frac{3}{4}$ in. It should be noted that the

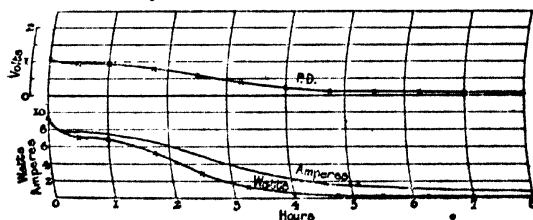


FIG. 53.—Discharge Curves of 3-pint Bichromate Cell, on same circuit as in Fig. 52.

area of the zinc was more than double that of the Benkő cell, and the carbon surface also much greater (though a little less in proportion). Yet when this cell was switched on to the same circuit as that which carried 12 amperes in

the test just referred to, the current, which rose momentarily to 9.6 amperes, fell quickly below 8 amperes, and continued to fall, as shown in Fig. 53. The P.D. and watts also fell rapidly. Even when a circuit of a higher resistance was used, giving an initial current of 6 amperes, the current fell off after a couple of hours. It is this characteristic which is so annoying to users of ordinary primary batteries, but which is so completely eliminated by the Benkö cell.

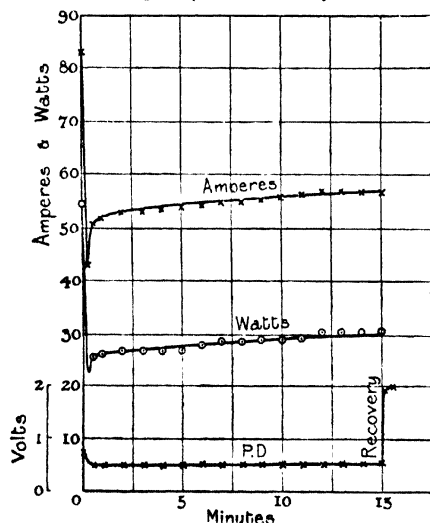


FIG. 54.—Heavy Current Test on Constant Resistance. Initial current, 8.3 amperes. Solution "P."

The test shown in Fig. 54 was made with a similar single cell, using the stronger solution P at a head (between the bottom of the tank and the top of the overflow tube) of 45½ in., which gave a flow of about 1.9 litres per hour. In this test the external resistance was maintained constant, and the fall of current was observed for 15 minutes. The

current might have been maintained longer, but the cell became very hot with such heavy discharges. Notwithstanding the severity of this test, the P.D. was maintained at about 0.55 volt. The current, after the initial drop, rose (doubtless due to the heating) to about 55 amperes, and the watts in the external circuit were about 30. For the size of cell this is a remarkable achievement.

Short-circuit tests with the L solution showed momentary currents of 100 amperes at a terminal voltage of 0.5 to 0.6 volt, the current falling to 80 amperes at the end of five seconds. With the stronger P solution, momentary currents of 200 amperes were taken at a terminal pressure of 0.5 to 0.55 volt. It follows, therefore, that the internal resistance is well below 0.01 ohm, an extremely low figure. This result is no doubt due largely to the excellent contact between the lead shell and the carbon.

Another type of Benkō cell has been developed, in which the electrolyte is no longer supplied under pressure, but passes through the carbon by diffusion.* The electrolyte, which in these cells may be made very concentrated, is run into the outer compartment, and plain water is run into the inner, or zinc, compartment. In a few moments the cell is ready for work. The great advantage of this type of cell is that the solution round the zinc is always only very slightly acid, and therefore local action is avoided; the zinc is dissolved away evenly when the cell is in use, and the depolariser is very thoroughly reduced. The efficiency, therefore, is high. An ampere hour efficiency in the neighbourhood of 90 per cent. is claimed for the zinc, which is much higher than for ordinary types of acid cell.

Supposing the level in the two compartments is the same initially, the specific gravity in the outer compartment may be, say, 1.3, compared with 1.0 (water) in the inner compartment. Consequently diffusion continues until there is

* "The Benkō Primary Battery," by W. R. Cooper, *Transactions, Faraday Society*, Vol. VII, p. 246, 1912.

equilibrium, whether the cell is in action or not. When the diffusion stops the cell becomes one of the ordinary type, polarisation sets in, and the current falls rapidly.

Obviously a cell of this kind cannot be used to give current continuously like the pressure type; the use for which it is intended may, perhaps, be described as semi-intermittent. For example, the Author has found that a cell weighing 5 lb. (including zinc, but excluding electrolyte), and having the dimensions $6\frac{3}{4}$ in. long, $1\frac{1}{2}$ in. wide and $6\frac{1}{4}$ in. high, gave a current for eight hours daily as follows (with initial P.D. of about 1.9 volts):—

First day	0.25 to 0.24 ampere.
Second „	0.25 to 0.24 „
Third „	Fell to 0.22 „
Fourth „	Fell to 0.20 „
Fifth „	Fell off seriously.

A current of 0.25 ampere is regarded as normal for this size of cell. The electrolyte amounted to about 200 c.c. and contained 170 grammes of sodium bichromate and 250 c.c. of sulphuric acid per litre. By using a more concentrated electrolyte the E.M.F. can be maintained longer.

The Benkö cell was placed on the market in Buda-Pest, but the Author is not aware whether it is still obtainable.

SPECIAL ELECTROLYTES FOR USE IN BICHROMATE CELLS.—The mixing of acid electrolytes is sometimes a matter of inconvenience to the user. To avoid this trouble J. J. Eastick & Sons, of London, supply in collapsible tubes solid excitant salts which are made ready for use by simply dissolving in the proper proportion of water. One of these excitants bears the name of “Chromolyte;” another is called “Chromic Acid,” and is stated to contain the necessary amount of sulphuric acid. Both the excitants are deliquescent.

Several patents have been granted for making dry mixtures of chromic acid and sulphuric acid. For example, according to patent No. 26,649 of 1909, by W. J. L. Sandy, a hard mass is made by mixing 32 oz. of anhydrous sodium

bichromate with 18.20 fluid oz. of concentrated sulphuric acid. Again, B. E. R. Newlands and R. M. Parkinson (patent No. 11,926 of 1909) mix 200 grammes of sodium bichromate, or the equivalent quantity of the potassium salt, with 125 cubic cm. of sulphuric acid; for use, this solid is dissolved in water, mixed with a solution of about 20 grammes of chloride, or other salt, of sodium, and diluted up to one litre. The use of common salt seems to be usual in all such formulæ, and the general proportions may evidently be varied rather widely, for W. H. Lowe makes a similar claim (patent No. 27,634) for a mixture of 28 oz. of anhydrous sodium bichromate and 18 fluid oz. of sulphuric acid.

Cells having Solid and Gaseous Depolarisers.

THE LALANDE CELL.—In this cell, due to De Lalande the electrolyte is a solution of caustic soda, and the depolariser is black oxide of copper, either supported upon,

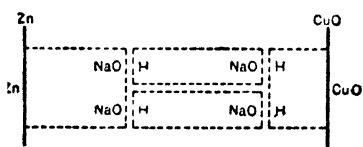


FIG. 55.—Reaction in the Lalande Cell.

or embodied with, the electro-negative plate. Copper oxide readily gives up its oxygen in the presence of a reducing agent, such as hyd-

rogen, and the copper so reduced easily takes up oxygen again and re-forms the oxide upon heating in the air. Its properties therefore render it eminently suitable for a depolariser.

When the cell is generating a current the zinc forms sodium zincate, which is soluble. The chemical reaction is represented diagrammatically in Fig. 55.

In one of the early forms of Lalande cell, the containing vessel was of iron and acted as the negative plate, a layer of copper oxide being spread over the bottom. The objection to this method of construction is that only part

of the negative plate is benefited by the depolarising action of the copper oxide. In another form the copper oxide was contained in an iron vessel which served as the negative plate, and was placed at the bottom of the ordinary glass jar.

A more recent form of this cell is shown in Fig. 56. The zinc, Z, is a cylindrical sheet, which, in the figure is broken away so as to show the inner cylinder, D, of perforated sheet iron which forms the negative plate. This cylinder contains the copper oxide, and is prevented from touching the zinc by cylindrical insulators, I I.

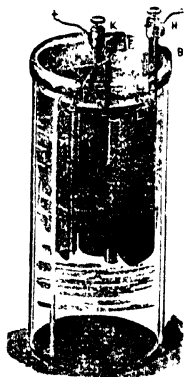


FIG. 56.—Lalande Cell.

This method of using copper oxide is not a very good one for obtaining electrical contact between the negative plate and the depolariser, and therefore the oxide is more often used in the form of an agglomerate plate. Such a cell, made by De Lalande, is shown in Fig. 57, in which Z is the zinc and C the copper oxide agglomerate held against a sheet-iron support by springs L, L, as shown in Fig. 58. The zinc and iron plates are held together by a rubber band K, but are prevented from touching by the ebonite insulators, I, I.

The method used by De Lalande in making the agglomerates is as follows:— "A wet mixture of copper scale and 4 to 5 per cent. of clay is submitted to hydraulic pressure, and baked at a temperature of 600° to 700°C.; or the scale may be mixed with 6 to 8 per cent. of tar, and, after moulding under pressure, placed in a reverberatory furnace. The oxide is in this way reduced, and the whole mass agglomerated. On exposure to the atmosphere the metallic plates oxidise again without any change of shape. The plates so

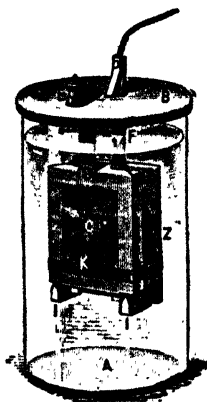


FIG. 57.—Lalande Cell with Copper Oxide Agglomerate.

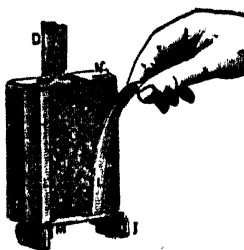


FIG. 58.—Method of Mounting Copper Oxide Agglomerate.

obtained are very strong and porous, but poorly conducting. This defect is mainly of importance when the cell first commences working, and to overcome it the agglomerate is metallised. A layer of powdered zinc is spread over the porous plate and the whole is plunged into slightly acid water, local action is set up, the zinc dissolves, and the surface of the oxide is reduced; but as it would re-oxidise

* *The Electrician*, Vol. XXVII., p. 166, 1891, from the *Bulletin de la Société Internationale des Electriciens*, Vol. VIII., pp. 219-226, 1891.

on drying, an extremely fine film of copper is electro-deposited, a large current density of short duration being employed."

THE EDISON-LALANDE CELL.—In this modification of the Lalande cell, which is shown in Fig. 59, the copper oxide is used in the form of plates such as those just referred to, but they are fixed in position in a slightly different way, viz., in a light copper framework which is attached to the cover of the jar, and also forms one of the terminals of the cell. Two zinc plates are used, one on

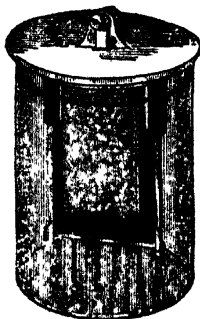


FIG. 59.—Edison-Lalande Cell.

each side of the copper oxide plate; they are fixed by a bolt passing horizontally through the central part of the cover which projects upwards for the purpose. The electrolyte is a solution of caustic soda, in the proportion of one part of soda to three of water by weight. This solution is prevented from being converted, through the action of atmospheric carbon di-oxide, into carbonate by the use of a layer of heavy paraffin oil which floats on the top.

Some curves showing the results of a test upon four Edison-Lalande cells in series, by A. E. Kennelly, are given

in Fig. 41, and the tests are referred to on page 146. The current is seen to be steady for a large proportion of the discharge.

In Fig. 60 is reproduced a discharge curve which the Author obtained from a cell supplied by the General Electric Company (London); it is known as Type A, having a diameter of $5\frac{1}{2}$ in. and a height of 8 in., with a capacity of 150 ampere-hours. The external resistance was a quarter of an ohm. It will be noticed that the current rises pretty rapidly when the circuit is first closed, owing to the reduction of oxide on the surface of the

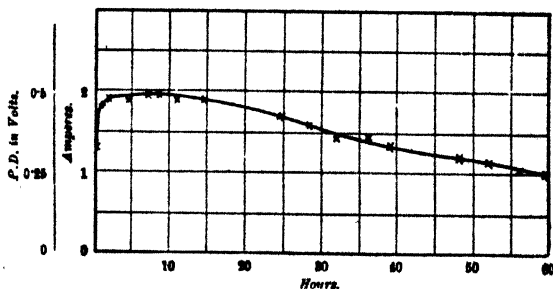


FIG. 60.—Discharge Curve of Edison-Lalande Cell, Type Q, through 0.25 ohm.

copper oxide plate, thus reducing the internal resistance. The current then becomes steady for a considerable time, after which it slowly falls.

The General Electric Company supply three sizes of this cell, having capacities of 150 (as above), 300 and 600 ampere-hours; they are very suitable for experimental work or the supply of power on a small scale—for example, to electric organs. There is no creeping of any salt, there is but slight local action, and there is no need for any attention. Local action takes place chiefly at the surface of the electrolyte, and is liable to cause the zincs to drop off before they are fully dissolved. There also appears to

be a tendency for the zincs to flake off even though amalgamated. The only serious disadvantage, however, is the low E.M.F. of the cell. When freshly set up, the E.M.F. may be as high as 1.0 volt or 1.1 volts, but the effective value is only about 0.75 volt. The cell is also rather expensive in first cost and in maintenance. It is not necessary, however, to discard the copper oxide plates when reduced by discharge. After soaking for a time in water to remove the excess of soda, they may be dried and re-oxidised by heating to a red heat in air. A large gas-burner may be used for this purpose; but in that case the plate should be protected from the direct action of the flame by a piece of thin sheet iron, otherwise reduction, instead of oxidation, is liable to take place in parts. A plate so treated is not likely to be so good as the original, and will give but a feeble current to start with unless previously reduced on the surface, but will nevertheless have a serviceable life. The simplest way to reduce such a plate is to short-circuit the cell for a few minutes. There also seems a tendency for the electrolyte eventually to crystallise through the earthenware jars.

Of the General Electric cells, the type Q (150 ampere-hours) is intended to discharge up to 1 ampere; type S (300 ampere-hours) up to 2 amperes and type W (600 ampere-hours) up to 4 amperes. Fig. 61 shows discharges of these cells on a 1 ohm circuit, the curves being based on data kindly furnished by the General Electric Co. It is seen that the power in the external circuit is generally a considerable proportion of the whole (that is, the P.D. does not fall unduly), which is important in any cell supplying current above what may be described as small (*e.g.*, 0.1 ampere).

The Thomas A. Edison Co. have now modified the design in their Edison BSCO cell, so that the three plates are sent out clamped together. By so doing, the clearance between the plates can be reduced to a minimum, thus minimising

the internal resistance and increasing the efficiency and capacity; and the plates are placed in position very easily.

The plates are separated by porcelain insulators and clamped together by an amalgamated steel bolt, as seen in Fig. 62. The makers state that by this design there is a gain of one-third in capacity and one-fifth in efficiency. These cells are used largely in the United States for railway track signalling. In this class of work it is desirable that the cell should not be much affected by temperature variations, nor freeze; the capacity should be large, so as to minimise attention, and the voltage should be constant on closed circuit. When a train passes over the section the

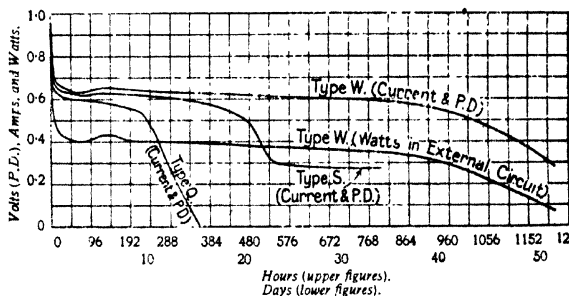


FIG. 61.—Discharge Curves of Edison-Lalande Cells, Types W, S and Q. Continuous discharge through 1 ohm, external resistance.

Type W:—600 amp. hrs. capacity: 15½ in. × 9 in. diameter.
 " S:—300 " " " 13½ in. × 5½ in. "
 " Q:—150 " " " 8 in. × 5½ in. "

cell is short-circuited, and therefore it is desirable to use it with a limiting series resistance so as to avoid waste. It is obviously important that cells so used should not come to an end of their life without some warning, and therefore the zincs are so proportioned that the lower panels become perforated when the cells are nearing the end of their life, as seen on the right-hand side of Fig. 62. The cells can be left in service until the holes become $\frac{1}{4}$ in. square.

Instead of running a resistance in series with the cells, the cells themselves may be so made that their internal resistance is sufficiently high to act as a safeguard. This is the case with the modified Lalande cell, known as the Columbia Track Cell* (made by the National Carbon Co.), in use in the United States. For this purpose the plates are more than usually separated, the zinc (amalgamated) being in cylindrical form suspended by three short wires, as seen in Fig. 63. The other plate lies at the bottom of the jar, and is made of a disc of tin plate, to which is riveted a rubber-covered copper wire to form the positive terminal. This plate is covered with flakey copper oxide, which is

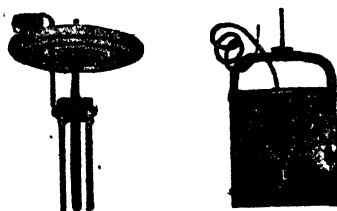


FIG. 62.—Plates of the Edison BSCO Cell.

poured in after the solution is made up. The caustic soda electrolyte is of specific gravity 1.25, and is largely in excess of the amount equivalent to the zinc, so that the sodium zincate formed by the action of the cell may be held in solution. As the zinc oxide becomes reduced to copper the red colour of the latter is visible through the glass, and affords a convenient indication of the extent to which the cell is discharged—a matter of importance in track signalling. Since the amount of copper oxide is so proportioned that it becomes used up before the zinc is all dissolved, there is no risk of unexpected failure if the oxide

* "A Railway Track Cell," by E. L. Marshall. *Transactions, American Electro-chemical Society*, Vol. XXV., p. 467, 1914.

is kept under observation. The jars are made of "heat-resisting" glass, so that they will withstand the heat due to dissolving the caustic soda. In the Columbia "Signal Cell" oil is incorporated in the copper oxide plate, and separates out when the element is plunged into the hot caustic soda, so that the addition of oil is unnecessary.

The "Neotherm" cell is another example of the copper oxide type, but it is much more robust in character. In this cell the container is an iron box, the inside of which is

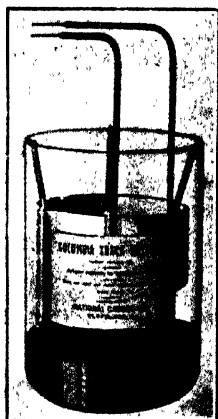


FIG. 63.—Columbia Track Cell.

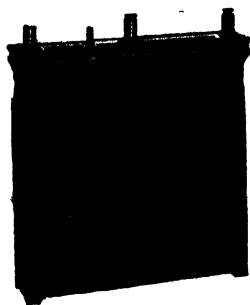


FIG. 64.
"Neotherm" Copper Oxide Cell.

coated with copper oxide, thus reverting to the original idea of De Lalande. In order to obtain a good coating the back and front inner surfaces are dentated, and copper is deposited upon them electrolytically. Specially prepared copper oxide is then pasted on these surfaces, and, after drying, it is "formed" by electrolysis, so as to be thoroughly porous. The cell is closed by an enamelled iron cover, which is fastened down by thumb screws. One of these serves as the positive terminal. The zinc is in

the form of a plate, and is provided with a brass stem; this screws into the centre terminal seen in Fig. 64, and which passes through an ebonite bush in the cover. The whole construction is thus very robust. The great advantage of the cell is that, after exhaustion, the electrolyte can be emptied out and the copper oxide rejuvenated by heating the container in an oven. In carrying out this operation, the oven is first brought to the required temperature (250°F.-300°F.), and any residue in the container is washed out by means of solution, it being important that water or other liquid should not be used for this purpose. As soon as this has been done the open container is placed in the oven, where it is left for a time varying from 3 to 6 hours, depending on the size of the cell. When the cell has cooled down after baking it may be recharged, and is then ready for use. The operation is stated to be quite simple, and any form of oven may be used for the purpose, provided the heat is not generated by burning gas inside the oven itself. The specific gravity of the caustic soda solution, when cold, should be 1.241.

This type of cell has been described by O. Arendt* as the Wedekind cell.

In making up the electrolyte, use should be made of caustic soda which is *ground*, as solution is then rapid. Caustic soda in large lumps dissolves but slowly to a strong solution, even in boiling water.

THE WALKER-WILKINS CELL.—This cell may be referred to here on account of its similarity to the Lalande cell in the use of caustic soda in the electrolyte, the copper oxide, however, being absent. The cell is of interest (although apparently it is no longer on the market), owing to the use of gaseous depolarisation, atmospheric oxygen being relied upon for this purpose. Fig. 65 shows an

* *Elektrotechnische Zeitschrift*, Vol. XXVII., p. 27, 1906.

elevation and a section of the cell. The zinc, in the form of a cylinder, or a spiral rod, in a solution of caustic soda, is supported in a porous pot, and this is contained in an outer perforated jar. The space between the two is occupied by a perforated nickel cylinder forming the negative plate, which is packed on the inner side with powdered, and on the outer with granular, carbon. The caustic soda, after passing through the porous pot, permeates through the carbon and slowly drains off into the earthenware stand. The depolarising oxygen is supposed to be absorbed by the carbon through the outer perforated vessel.

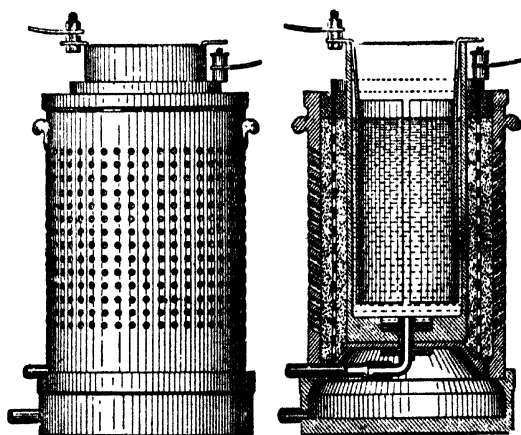


FIG. 65.—Walker-Wilkins Cell.

It was at one time suggested that this cell should be used for the supply of electricity for lighting purposes, zinc oxide being obtained as a bye-product. But the project fell through. For general laboratory work the cell is in many ways unsuitable: it is rather complicated it requires attention, because the caustic soda is continually draining off and carbonating; and, lastly, if it is allowed to get dry, the porous pots are likely to split.

The E.M.F. varies up to about 1·4 volts, but the effective E.M.F. is probably less than 1 volt.

THE HARRISON CELL.—The use of lead peroxide as a depolariser is well known in connection with accumulators, but it has never been used to any large extent in primary batteries owing to the difficulty of making plates that will

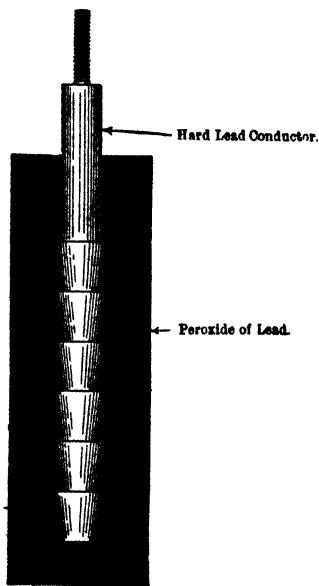


FIG. 66.—Negative Rod of Harrison Cell

last. This difficulty appears to have been overcome in the Harrison cell, which has been introduced in America. Electrolytically prepared lead peroxide, subjected to a secret process, is compressed round a central conductor of hard lead which has been previously treated in a way that prevents sulphating when in use. The section of such a rod is shown in Fig. 66.

As the electrolyte is dilute sulphuric acid it is necessary to have the zinc always well amalgamated in order to avoid local action. The way in which this is effected is of some interest. The zinc is cast in the form of a cup and is attached to an amalgamated wire forming the terminal, as shown in Fig. 67. Into this cup, and round the copper wire, enough melted zinc amalgam is poured to completely

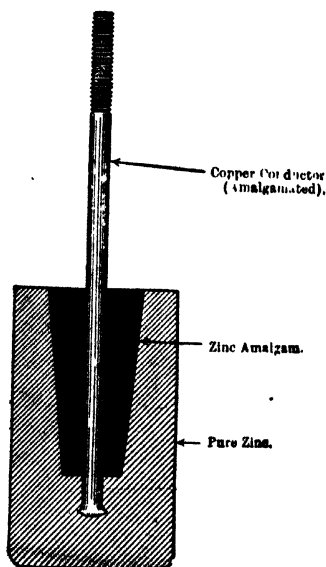


FIG. 67.—Positive Block of Harrison Cell.

fill it. Since this amalgam is solid when cold there is no free mercury to give trouble by loss in transit. No further amalgamation is necessary. When the zinc is placed in the acid, local action will, of course, take place on the surface of the unamalgamated zinc; and since zinc amalgam is slightly electro-positive to pure zinc, local action will also take place on the surface of the

amalgam. This latter local action, however, liberates mercury, which spreads over the whole of the unamalgamated surface until the amalgamation is complete and the local action is stopped. The placing of the amalgam in a cup in this way at the top of the zinc is an important feature, as it prevents the gravitational separation of mercury, which generally causes the amalgamation of vertical zinc plates to be so ineffective.



FIG. 68. — Harrison Cell, No. 1.

This form of zinc is intermediate between a plate of zinc amalgamated on the surface and a plate of zinc amalgam, *i.e.*, with mercury throughout. Amalgamation on the surface is very effective when fresh, but the protective action diminishes as solution takes place and as impurities collect in the mercury. With a plate of amalgam, on the other hand, the amount of mercury on the surface increases as solution continues, and therefore the amalgamation remains effective; but such plates are more brittle than those of zinc and are more expensive.

If impure sulphuric acid is used, local action is still liable to occur, notwithstanding the amalgamation, owing to the deposition of less electro-positive metals by the zinc. In the case of metals which readily amalgamate, such as copper, no harm results; but if such metals as iron, arsenic and selenium are deposited on the zinc, they do not amalgamate, and local couples are therefore formed. This state of things is easily remedied, after

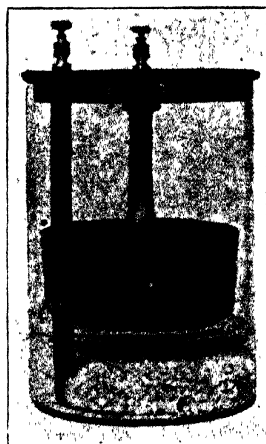


FIG. 69. — Harrison Cell. No. 3.

complete deposition has taken place, by scrubbing the impurities off the surface in running water. A solution of bisulphate of potash or soda gives almost as good a result as sulphuric acid.

Fig. 68 is an illustration of the smaller size of Harrison cell, in which the cylinders of peroxide and of zinc are placed side by side. This cell is intended to supply only small currents. In the large cells the arrangement shown in Fig. 69 is adapted. Granulated zinc, placed on a copper

grid at the bottom of the jar, is used in place of the cylinder previously described. Connection is made with the grid by means of an insulated copper wire. To prevent local action, a quantity of mercury is placed at the bottom of the jar. This method of utilising granulated zinc has the great advantage that waste zinc is completely avoided.

The lead support of the peroxide is in the form of a basket or grid, divided internally into four equal parts by

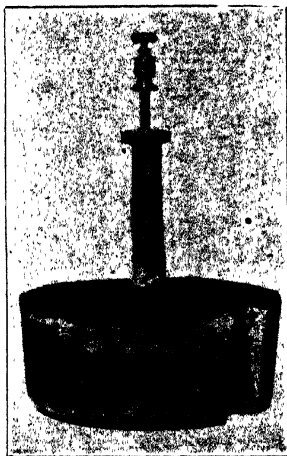


FIG. 70.—Lead Peroxide Plate.

lateral walls, and supported by a central rod passing through the cover of the cell and forming the positive terminal. This is shown in Fig. 70.

One great advantage of the Harrison cell is its high E.M.F., viz., 2.5 to 2.7 volts.

In Fig. 71 are reproduced curves obtained by J. D. Darling* in testing two No. 1 cells in comparison with two sal-ammoniac cells containing manganese peroxide and two

* *Journal of the Franklin Institute*, Vol. 148, pp. 55-55, 1899.

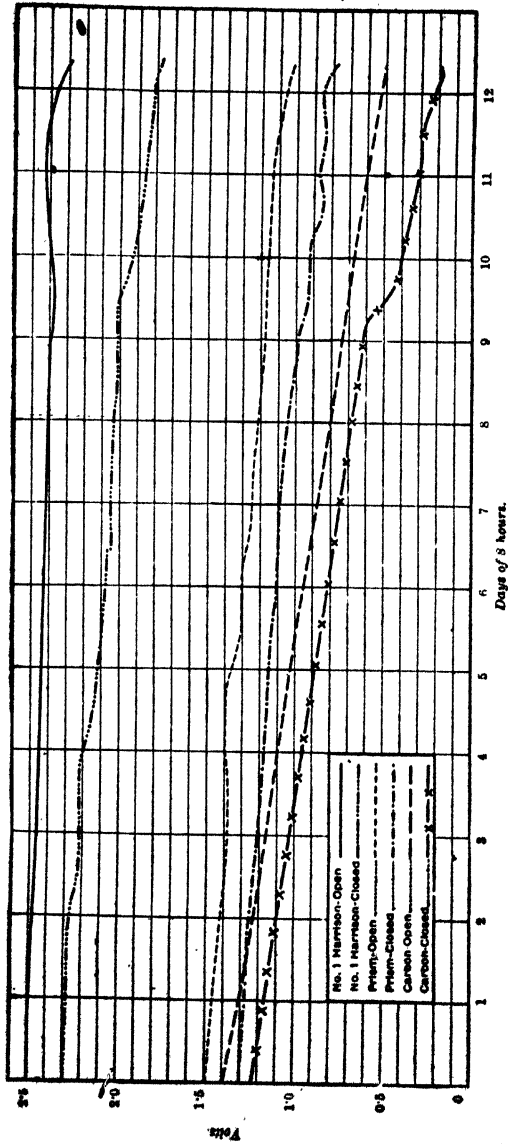


FIG. 71.—Comparative Discharge Curves of Harrison and other Cell through 8 ohms, alternately opened and closed for five minutes.

plain carbon cells without a depolariser. Half the cells were left on open circuit, each of the remaining cells being placed on a circuit of 8 ohms. These circuits were alternately opened and closed for five minutes during twelve days of eight hours each. Initially the E.M.F. of each cell was as follows:—Harrison cells 2·5 volts; sal-ammoniac cells (depolarising) 1·5 volts; plain carbon cells 1·4 volts. At the end of the tests the "E.M.F. on closed circuit" (by which P.D. is probably intended) was as follows: Harrison cell 1·8 volts; sal-ammoniac cell (depolarising) 0·8 volt; plain carbon cell 0·2 volt. Nothing is stated as to the size of the sal-ammoniac cells. Considering the small size of the Harrison No. 1 cell, viz., 6in. high over all by 3in. square, the result appears to be fairly satisfactory, though probably not so good as that obtainable from an Edison-Lalande cell. The Author is not aware whether the cell is still on the market.

BELLINI'S CELL.—E. Bellini* has pointed out the desirability of avoiding any possibility of depositing ions of the electro-positive metal on the electro-negative element, where a single electrolyte is used. For example, in the case of the simple cell, consisting of platinum and zinc in dilute sulphuric acid, zinc tends to be deposited on the platinum as zinc sulphate forms in solution, and thus leads to increasing polarisation. In order to avoid this difficulty Bellini uses a metal for the electro-positive plate which forms an insoluble salt. Lead in sulphuric acid is therefore selected. If plain lead is used it becomes coated with sulphate, and the internal resistance becomes too high for useful work. To overcome this difficulty the lead is amalgamated, in the proportion of one part of mercury to nine of lead. The amalgamation is effected by melting the lead, adding the mercury to the molten metal when not too hot

* *The Electrician*, Vol. LXXIV., p. 809; *Bulletin, Société Internationale des Electriciens*, Vol. V., p. 35, 1915.

and stirring, after which the amalgam is poured into a mould of the required form. The other plate of the cell is carbon, and the electrolyte is a mixture of sulphuric and nitric acids.

The action of the cell is interesting, and is shown diagrammatically in Fig. 72. We may look upon the sulphuric acid and nitric acid as acting in parallel, but it is immaterial whether we suppose the lead to be attacked by the SO_4 forming PbSO_4 directly, or by the NO_3 forming $\text{Pb}(\text{NO}_3)_2$, because the nitrate, if so formed, will at once react with the sulphuric acid to form insoluble sulphate. Thus lead sulphate is formed, and as this does not become attached to the amalgamated surface it falls to the bottom of the cell. At the carbon plate the polarising ion can

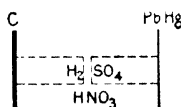


FIG. 72.—Representation of Bellini's Cell.

only be hydrogen, and this is removed by the nitric acid, which acts as a depolariser as usual. Gas is thus given off at the carbon plate, and analysis shows this to be chiefly nitrogen, along with some oxygen, carbonic acid and oxides of nitrogen. It becomes clear that if only sulphuric acid is used polarisation must be heavy owing to the absence of a depolariser; on the other hand, if there is only nitric acid, lead nitrate will be formed, and, as this is soluble, lead will in time find its way to the carbon plate, and will cause polarisation. The mixture is, therefore, essential. The inventor mentions the following as being a satisfactory formula :—

	Parts by volume.
Sulphuric acid, sp. gr. 1·8	2
Nitric acid, sp. gr. 1·3	3
Water	25

The E.M.F. is 1.1 to 1.25 volts, and the discharge obtained is constant over a number of hours. This is shown by the curves in Fig. 73 as given by Bellini. These refer to a cell containing 2.6 litres (about 2½ quarts) of electrolyte, three lead amalgam plates with a total immersed area of 900 sq. cm. (139½ sq. in.) and four carbon plates with a total immersed area of 1,230 sq. cm. (190½ sq. in.). The cell, therefore, was rather large, and had an internal resistance of 0.022 ohm. The curves show two successive discharges through a constant resistance, with an interval of 10 hours' rest between them, on a single charge. It is seen that

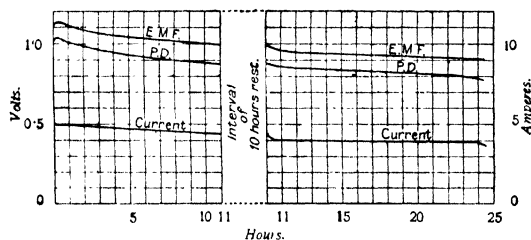


FIG. 73.—Discharge Curves of Bellini Cell on Constant External Resistance.

the current fell from 5 amperes to 4 amperes in a total discharge of 25 hours. The local action is stated to be small.

SILVER CHLORIDE CELL.—This cell, apparently due to O'Shaughnessy, was at one time used as a standard of E.M.F. It was also brought into prominence by researches on disruptive discharge by De la Rue, whose name it sometimes bears; but it is now seldom employed. A dry form, however, has been used in recent years in America for medical purposes. The cell usually consists of zinc and silver as electrodes in a solution of either common salt, zinc

chloride or ammonium chloride. The silver chloride, which is reduced by hydrogen to silver, acts as a depolariser. The silver chloride is either placed in the form of powder at the bottom of the cell as a covering to the silver plate, or, preferably, it is fused in the form of a rod round a silver wire which is used as the electrode. The internal resistance of such cells is not very high when new, but it increases rapidly owing to the formation of oxychloride on the zinc. This may be remedied by adding a very small quantity of hydrochloric acid. Such cells, however, are generally troublesome. The E.M.F. is about 1.05 volts.

SULPHATE OF MERCURY CELL.—This cell, like that just described, is used for medical purposes, such as the working of small induction coils. The plates are zinc and carbon. Acid mercuric sulphate is used as a depolariser. This enters sufficiently into solution to give a suitable electrolyte. For medical purposes the carbon is usually set in the bottom of a vulcanite case. The mercuric sulphate is placed on the carbon along with a little water, and the zinc plate is laid on top. The E.M.F. is about 1.45 volts. The cells are frequently made two in series, the zinc plates automatically making the necessary connections with platinum wires when put into position.

Leclanché Cells.

THEORY OF LECLANCHÉ CELLS.—Most of the cells which have so far been considered are provided with effective means for depolarisation, and are therefore capable of generating heavy currents. We now come to a very large class which has sprung from the cell introduced in 1868 by Leclanché, and which was originally characterised by feeble depolarising qualities. Its popularity is due to its simplicity and to the small attention which it requires. These properties are very important in certain classes of

work—for example, on bell and telephone circuits; for where only intermittent currents are required, good depolarisation may become relatively unimportant. Of late years the depolarising qualities have been much improved, thus permitting heavier currents.

The Leclanché cell consists essentially of a zinc and a carbon plate, the latter being in contact with the depolariser, which is manganese peroxide in some suitable form. The electrolyte is generally a solution of sal-ammoniac (ammonium chloride), but other excitants, which are trade secrets and are specially made by combining ammonium chloride with other salts, are sometimes used.

The chemical reaction which takes place when a current is generated may be represented as shown in Fig. 74.

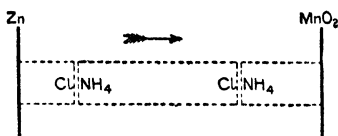


FIG. 74.—Voltaic Reaction in the Leclanché Cell.

Zinc chloride is formed on the surface of the zinc, and the ammonium radicle passes into contact with the manganese peroxide. The ammonium breaks up into free ammonia and hydrogen, the latter causing polarisation. Since MnO_2 readily reduces to Mn_2O_3 , this hydrogen is converted into water, and its polarising influence is eliminated so long as it is not produced more quickly than the reducing action can take place. The free ammonia also causes a lowering of the E.M.F., as shown by M. de Kay Thompson and E. C. Crocker.*

The E.M.F. of a Leclanché cell is about 1.5 volts, but this soon drops when on circuit, so that it is necessary

* *Transactions, American Electro-Chemical Society*, Vol. XXVII., p. 155, 1915.

to regard the effective E.M.F. as being about 1 volt in estimating the number of cells required to furnish a given current, unless the current required is very small.

THE POROUS POT FORM OF CELL.—The form of Leclanché cell which is most commonly used is that in which the depolarising manganese peroxide is contained in a porous pot. Such a cell is shown in Fig. 75. The carbon plate is fixed in the porous pot and is packed round with granular peroxide, mixed with broken gas carbon to

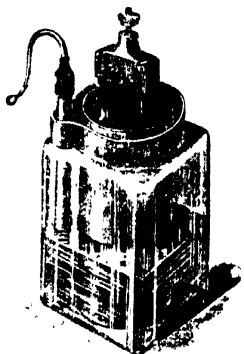


FIG. 75 —Porous Pot form of Leclanché Cell.

increase the conductivity and to make good contact with the carbon plate; at least, this is so in the more ordinary types, but in the more recent types the ingredients have been of much smaller grain, and in cells made for the Post Office the manganese peroxide is powdered, as described later. The pot is sealed up with a mixture of black wax and pitch, into which two small vent tubes are inserted to allow the liberated ammonia to escape.

The positive plate consists of a single zinc rod, with a copper connecting wire soldered to the top.

There are three obvious objections to this form of cell. Firstly, the use of a porous pot introduces resistance. This cannot be very well avoided where fluids have to be separated, as in the case of two-fluid cells; but a Leclanché cell contains only one electrolyte, and, therefore, the porous pot merely serves to keep the solid depolariser in position, and is otherwise not essential. Secondly, the use of a single rod of zinc, and likewise the porous pot, must cause the internal resistance to be comparatively high. Thirdly, the cell is open and is therefore liable to give trouble on account of evaporation.

The electrolyte is made up by dissolving sal-ammoniac in the proportion of from 2 oz. to 4 oz. of the salt to a pint of water. If this solution is poured only into the outer jar it will diffuse through the porous pot but slowly, and therefore the cell will not be ready for use until the next day. But if the solution is also poured down the vent tubes the cell will be ready in a comparatively short time. Porous pots are sometimes made with three or four saw-cuts at the bottom so as to allow a ready penetration of the electrolyte.

Cells may often be seen with an excess of sal-ammoniac crystals at the bottom of the cell, but such a practice is objectionable, as it leads to a deposit of crystals on the zinc which interferes with the voltaic action. Probably the most satisfactory strength of solution for general use is made by dissolving 3 oz. of the salt in a pint of water, but if a considerable current is desired the solution should be saturated.

Porous pot cells are made in three sizes—viz., pint, quart and 3-pint. Discharge curves obtained by running cells of this kind on a 10-ohm circuit are shown in Fig. 76, and were supplied to the Author by the India Rubber, Gutta Percha & Telegraph Works Co. (frequently called the Silver-town Co.). Curve A refers to a 3-pint cell. It will be seen

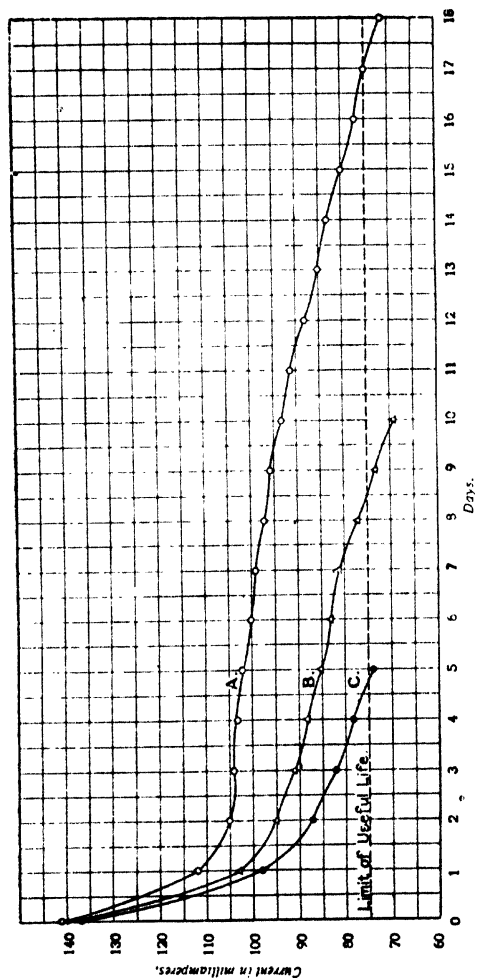


FIG. 76.—Discharge Curves of "Silvertown" Leclanché Cells. Porous Pot Type. Continuous Discharge through 10 ohms.

(Electrolyte, ammonium chloride saturated, at 55°F.)

Curve A.	" Silvertown "	3-pint cell,	Porous Pot	Type	Internal resistance—0.60 ohm.
" "	" "	" "	" "	" "	" =0.70 ohm.
" B.	" "	" "	" "	" "	" =0.85 ohm.
" C.	" "	One-pint cell	" "	" "	" "

that the current dropped to half its nominal maximum possible value—viz., to 75 milliamperes—in 17 days. The fall of current is very rapid at first, showing that the cell is unsuitable for a continuous discharge of this kind.

Curve B was obtained from a quart cell, also by the Silvertown Company, and curve C refers to a similar pint cell. The useful life was $8\frac{1}{2}$ days in the former and $4\frac{1}{2}$ days in the latter. These curves are typical of high-class porous pot cells in which the granular size of manganese peroxide is used.

In testing Leclanché cells, the useful life is considered to be the time required for the current to fall to half its nominal maximum possible value; for example, to 75 milliamperes on a 10-ohm circuit, or when the voltage has fallen to half the nominal E.M.F. (*i.e.*, 0.75 volt). The reasons for selecting this limit were discussed on page 141. Thus, in Fig. 76, the useful life of each cell is given by those parts of the curves which lie above the horizontal dotted line.

Figs. 77 and 78 are reproduced from curves supplied by Messrs. Siemens Brothers & Co., showing the discharge of their improved 3-pint and quart porous pot Leclanché cells compared with the ordinary type of cell. In this improved type powdered manganese peroxide is used on the lines specified by the Post Office, as described at the end of the present chapter. The manufacture of such cells is more expensive and, therefore, the price is appreciably higher, but the output is considerably greater. The increased output is shown by the curves and by the following figures which are deduced from them :—

Size of cell.	Size of porous pots.	Output in Ampere-hours, down to		
		1 volt.	0.75 volt.	0.5 volt.
Improved pattern } 3-pint ...	$6\frac{1}{2}'' \times 3''$	37.0	79.6	85.4
Ordinary pattern }		25.3	29.5	33.2
Improved pattern } Quart ...	$5\frac{1}{4}'' \times 2\frac{1}{2}''$	14.4	39.7	51.8
Ordinary pattern }		12.4	17.6	19.9

In these tests ordinary drawn zincs were used and a saturated solution of sal-ammoniac. The curves also show the rise of internal resistance as the discharge proceeds.

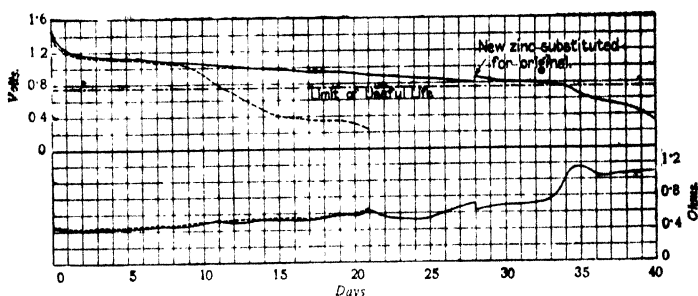


FIG. 77.—Discharge Curves of Porous Pot Leclanché Cells (3 pint size). Continuous Discharge through 10 ohms, external resistance.

————— Siemens Improved Pattern.
 Ordinary Pattern.

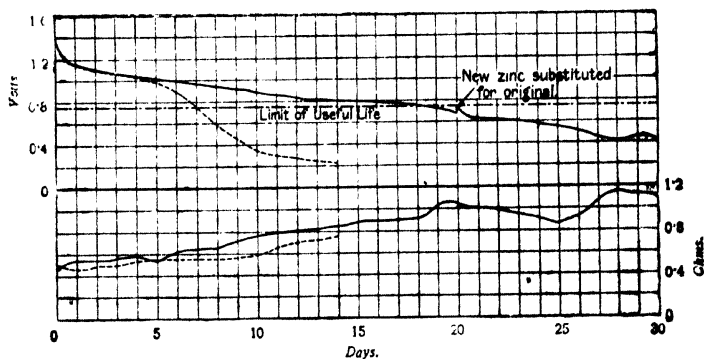


FIG. 78.—Discharge Curves of Porous Pot Leclanché Cells (quart size). Continuous Discharge through 10 ohms, external resistance.

————— Siemens Improved Pattern.
 Ordinary Pattern.

The curves in Fig. 79, which were obtained by the Author several years ago, are of interest as showing the effect of rest and discharging, and also as evidence of the improvement that has taken place since that time. If allowed to rest after discharge, a Leclanché cell recovers its E.M.F. fairly rapidly at first, and then rises slowly to a value which is somewhat lower than the initial E.M.F. For example, the discharge of a 3-pint cell is shown by the curve A and of a quart cell by curve B. These cells after discharge were allowed to rest, when it was found that the E.M.F. of cell A rose to 1.4 volts after 74 days, and cell B reached 1.42 volts after 87 days. After a recovery of this kind the cells are capable of a further discharge, but it is comparatively short, as shown by curves A' and B'. These curves relate to cells made by the Silvertown Co. about 1898, and should be compared with the present-day curves in Fig. 76 to appreciate the progress that has been made in the interval. The discharge of another quart cell by a different maker is shown at C.

When exhausted, a Leclanché cell may be recharged with fresh solution, but the E.M.F. is not so high as that of a new cell, and the useful discharge is always very much less. Such a discharge is shown in curve C', which was obtained by recharging cell C after the current in the first discharge had fallen to 55 milliamperes. It will be noticed that the current fell to 75 milliamperes in about one-fifth of a day, and therefore the useful life by such a recharge is comparatively small. It becomes necessary to renew the porous pot if a good result is desired; the zinc also is of comparatively little use after a cell has been run down, as it generally becomes rotten.

THE AGGLOMERATE BLOCK CELL.—The first defect mentioned above is overcome to some extent in the agglomerate block cell in which the porous pot is absent. This

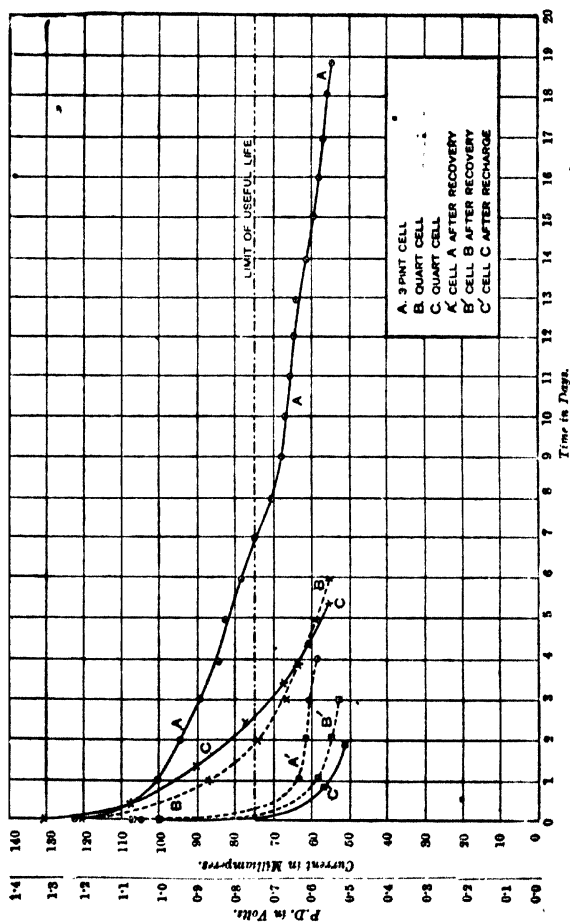


FIG. 70.—Discharge Curves of the Poreus Pot form of Leclanché Cell, discharged through 10 ohms (1898).

is effected by making the mixture of carbon and peroxide into agglomerate blocks with some binding material, such as resin or a little shellac, and left unbaked. These blocks are placed one on each side of the carbon plate, and are held in position by strong rubber bands. The arrangement is clearly shown in Figs. 81 and 82. Le Carbone, in some of their cells, have used bolts instead of rubber bands for holding the various parts together, the heads of the bolts

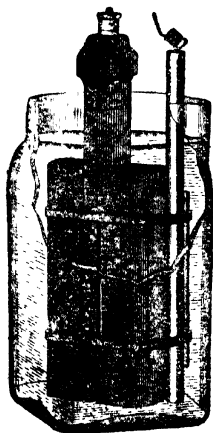


FIG. 80.—Agglomerate Block Cell.

taking the place of the insulator which usually carries the zinc. Some makers replace this insulator by a small loose porous pot, in which is placed the zinc rod.

In the form of cell shown in Fig. 80, the zinc rod is placed in a porcelain insulator, the zinc, insulator and blocks being all held in position by the rubber bands. But if the cell is closed by a lid to prevent evaporation,

the insulator may be omitted, as seen in Fig. 81, which represents a cell made by Leclanché et Cie. ; the zinc rod in this case is held in position sufficiently by the lid through which it passes.

In Fig. 82 are reproduced curves supplied to the Author by the Silvertown Company and obtained by discharging agglomerate block cells through a resistance of 10 ohms. Curve A refers to a 3-pint cell, and curve B to a quart cell, both made by the Silvertown Company. A comparison between these curves and those in Fig. 76 show that, as far

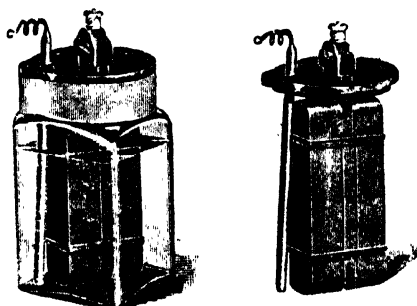


FIG. 81.—Method of Fixing Agglomerate Blocks.

as life goes, the agglomerate block cell is inferior to the porous pot form of cell. For example, the 3-pint agglomerate gave a life of $10\frac{1}{4}$ days, as compared with 17 days for the porous pot cell. In the case of the quart size, the life was five days for the agglomerate, as compared with $8\frac{1}{2}$ days for the porous pot cell. It may be said that in recent years there has been greater progress in the porous pot form than in the agglomerate. On the other hand, the latter type is less liable to deterioration by clogging and risk of breaking, and perhaps more uniform.

Another form of agglomerate block cell, known as the Aylmer-Leclanché cell, made by Leclanché et Cie., is

shown in Figs. 83 and 84. It is intended for a higher rate of discharge, and to this end the internal circuit is much improved by having, in place of a zinc rod, a cylinder of zinc surrounding the agglomerate blocks. A semi-cylindrical block is placed on each side of the carbon plate and is held in position by three rubber bands as indicated in Fig. 84, in which the zinc is shown cut away so that the arrangement of the blocks may be more clearly seen. The distance between the agglomerate blocks and the zinc is



FIG. 83.
Aylmer-Leclanché Cell.



FIG. 84.
Construction of the Aylmer-
Leclanché Cell.

but little more than the thickness of the rubber bands. Consequently the internal resistance is a good deal smaller than that of the cells just described, being about 0.2 ohm for a cell 10in. high and 5in. diameter.

Fig. 85 shows a similar cell having an ebonite jar which is closed in at the top, and is therefore convenient for portable purposes.

In Fig. 82 curve C shows the discharge obtained from an Aylmer-Leclanché cell on a 10-ohm circuit. The useful life in this case was about 7.4 days. A similar type of cell

is made by the Silvertown Company and Siemens Brothers & Co., and is known as the 6-Block Agglomerate Cell. It consists of six agglomerate cylinders which fit against a central fluted carbon rod, as shown in Fig. 86. They are wrapped round with coarse canvas, C, and are further held in position by rubber bands, R, which also serve to separate the agglomerate blocks sufficiently from the cylindrical zinc plate. Curve C in Fig. 82 was obtained by discharging a 3-pint cell of this kind on a 10-ohm circuit. The result



FIG. 85.
Sealed pattern of
Aylmer-Leclanché
Cell.

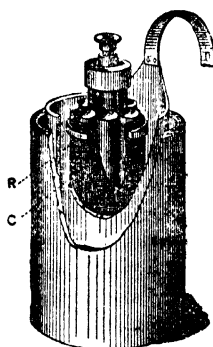


FIG. 86.
Six-Block Agglomerate
Cell (Silvertown Company).



FIG. 87.
Le Carbone "Star"
Agglomerate Block.

is seen to be very satisfactory, a useful life of 18 days having been obtained. In Fig. 97 is given the discharge curve of a similar cell by Siemens Brothers & Co. Here the life was 23 days. A curve is also given showing the variation of the internal resistance in this case, from which it is seen that the resistance at first rises steadily and then remains constant.

Le Carbone have also used a form of agglomerate consisting of a carbon box holding the mixture of carbon and

peroxide, the top and bottom of the box being closed with a bituminous seal. This type of construction is illustrated in Fig. 87. It would seem to be a disadvantage (at least theoretically) that the outside of such a box cannot act as an electrode, owing to its polarised condition; it is necessary for the current to pass to the inside of the box before depolarisation can take place.

CENTRAL ZINC CELLS.—The best known example of this class of cell is the Leclanché-Barbier, which is made

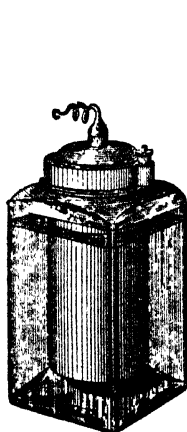


FIG. 88.—Leclanché-Barbier Cell.

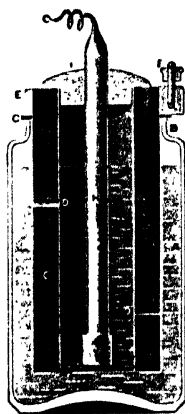


FIG. 89.—Section of Leclanché-Barbier Cell.

by Leclanché et Cie., and was designed particularly to eliminate evaporation. A general view of the cell is shown in Fig. 88 and a section in Fig. 89. There is no carbon plate, its place being taken by a hollow cylindrical agglomerate, C, of plumbago and peroxide, round the top of which is cast a metal ring, E (Fig. 89). This ring carries the terminal F and rests on the top of the jar, a rubber

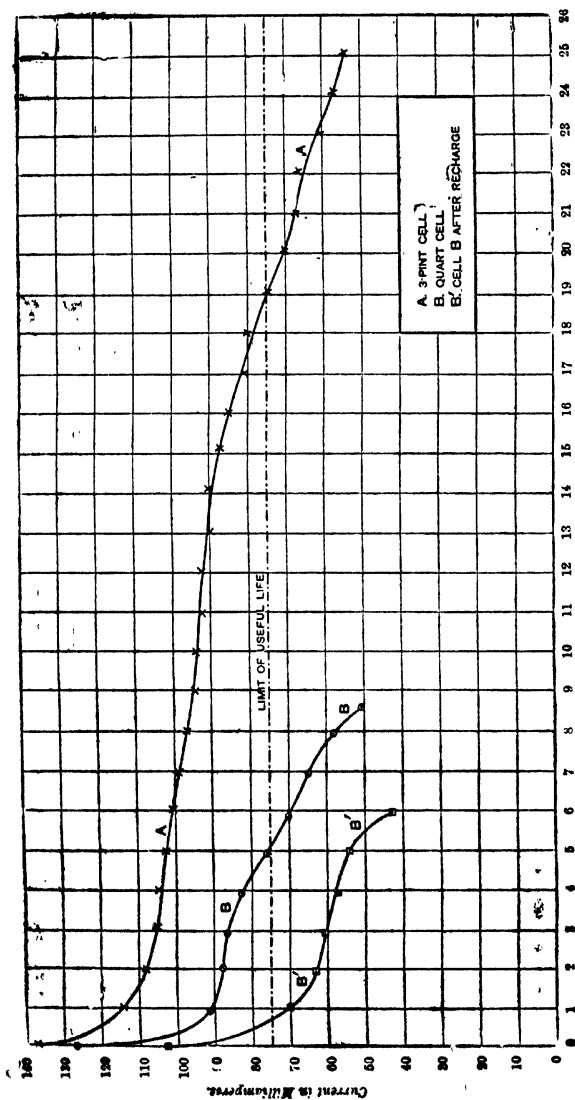


FIG. 90.—Discharge Curves of Leclanché-Barbier Cells, discharged through 10 ohms.

washer, G, being interposed to make an airtight joint. The zinc rod is supported by a paraffined wooden stopper, I, and carries a rubber band, J, at its lower end to prevent accidental contact with the agglomerate. The cell is thus completely closed, and evaporation, as also creeping of the salt, is entirely prevented.

The agglomerate in this cell contains a considerable proportion of graphite as well as peroxide and carbon. In order that the depolarisation should be effective, it is necessary that it should take place throughout the block and not merely at the surface. The required porosity is obtained by adding a small quantity of sulphur; the mixture is pressed into shape and then baked, when the sulphur volatilises, leaving an agglomerate that is exceedingly porous.

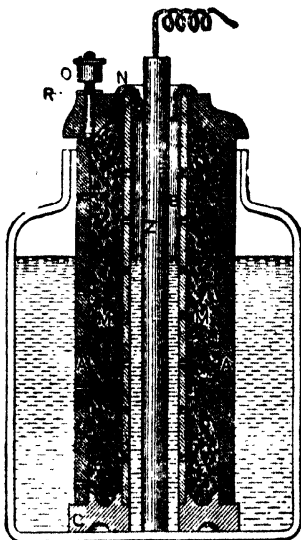


FIG. 91.—Section of Lacombe Cell.

Fig. 90 shows two discharge curves which were obtained by the Author. Curve A refers to a No. 1 cell (3-pint size) which was discharged on a 10-ohm circuit. The result is very satisfactory, showing a life of 19 days. Curve B refers to a No. 2 cell (quart size) which was run under the same conditions. In this case the useful life was 5.1 days. On recharging, this cell gave an E.M.F. of 1.17 volts, which slowly rose to a steady value of

1.37 volts after about a fortnight. The useful life resulting from this recharge was only 0.7 of a day, as shown by curve B'.

Another form of central zinc cell is the Lacombe cell (made by Le Carbone), of which a section is given in Fig. 91. It consists of a perforated carbon cylinder, A, with a head which carries the terminal O. Within the carbon is a second perforated cylinder, B, of porous porcelain. Both cylinders rest upon a glass base, C, and the annular space between them is filled with the depolarising mixture. The zinc Z is placed within the porcelain cylinder on the top of which is a circular insulator, N.

SACK CELLS.—During recent years there has been a considerable development of so-called "sack" Leclanché cells. These cells are essentially the same as the porous pot form, except that the porous pot is replaced by canvas. The construction of the electro-negative element in this form is illustrated in Fig. 92, which refers to the "Carbi" cell of Le Carbone, one of the earliest makers of this type. At the bottom the canvas is bound tightly round a wooden base; at the top the canvas is turned over and is finished off with a bituminous layer round the carbon. Fig. 93 shows the construction adopted by Messrs. Siemens Brothers & Co.



FIG. 92.
"Carbi" Sack,
as made by Le
Carbone.

The use of canvas in this way appears to permit the better utilisation of the depolariser, and results in a lower internal resistance (both initially and during discharge, presumably because there is less clogging) than is obtainable with a porous pot. Also the carbon and peroxide can be used in a finer powder

and rammed more tightly round the carbon plate. Consequently the larger cells of this type are capable of giving a comparatively heavy service, and may be used for the lighter classes of "closed circuit" work.



Electro-negative element with porcelain cover.



Electro-negative element sealed with compound.

FIG. 93.—Electro-Negative Elements of Siemens Sack Cells.

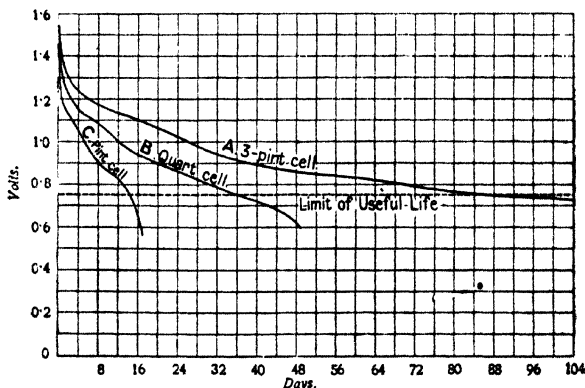


FIG. 94.—Discharge Curves of G.E.C. Sack ("Carsak") Cells. Continuous Discharge through 10 ohms external resistance.

Pint	7½ in. × 4 in. × 4 in.,	Internal resistance = 0.12 ohm.
Quart	7½ in. × 4½ in. × 4½ in.	" " = 0.10 ohm.
3-pint	8½ in. × 4½ in. × 4½ in.	" " = 0.08 ohm.

The General Electric Co. (England) was also early in the field in developing a sack cell, known as the "Carsak." Discharge curves (supplied to the Author by the General Electric Co.) of these cells are given in Figs. 94 and 95. Fig. 94 refers to the three smaller sizes discharged through 10 ohms. If a resistance of 10 ohms were used for testing the larger sizes, the tests would be unduly prolonged; consequently Fig. 95 refers to tests on a 5-ohm circuit.

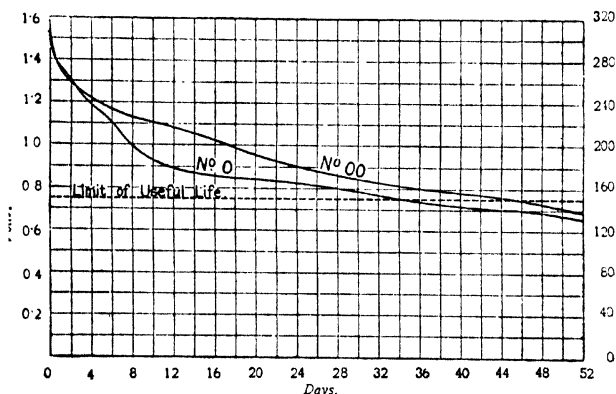


FIG. 95.—Discharge Curves of G.E.C. Sack ("Carsak") Cells Nos. 0 and 00. Continuous discharge through 5 ohms external resistance.

No. 0, 2-quart size, 9 in. \times 5 in. diam., int. resist., 0.05 ohm.
 No. 00, 5-pint size, 10 $\frac{1}{4}$ in. \times 5 in. diam., int. resist., 0.05 ohm.

In Figs. 96 and 97 is given a series of curves, which were supplied to the Author by Messrs. Siemens Brothers & Co., referring to the four sizes of sack cell made by this firm. Nos. 1, 2 and 3 sizes of cell are rather smaller than the 3-pint, quart and pint sizes of the porous pot type, yet it is seen on reference to Figs. 77 and 78 that the useful life is considerably greater for the sack form. A corresponding curve for a 6-block agglomerate cell is also given.

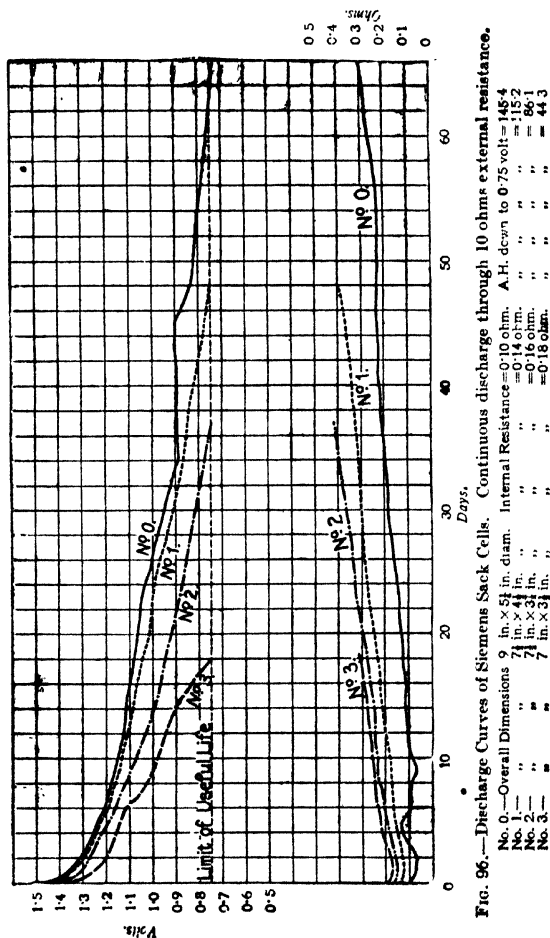


FIG. 96.—Discharge Curves of Siemens Sack Cells. Continuous discharge through 10 ohms external resistance.

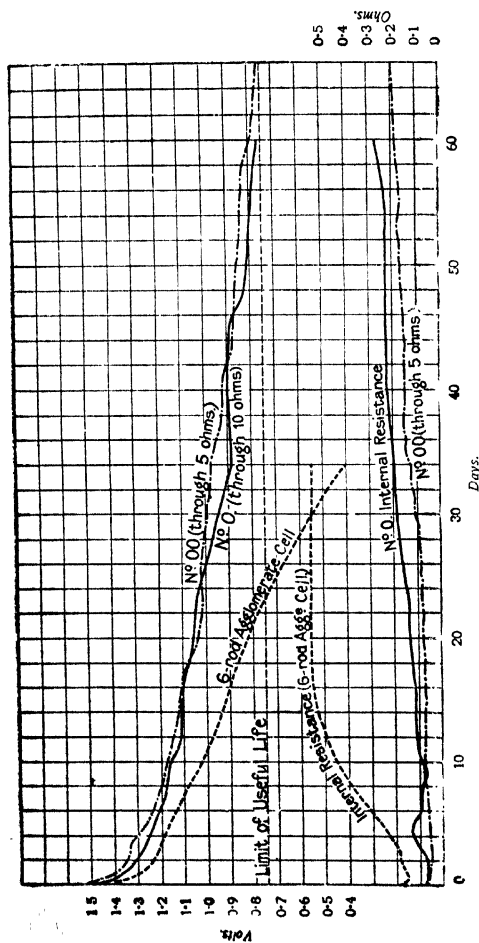


FIG. 97.—Discharge Curves of Siemens Sack Cells and 6-rod Agglomerate. Continuous discharge through 10 ohms external resistance except No. 00 (through 5 ohms).

The No. 0 cell is a larger cell than the No. 1. The No. 00 cell is of the same diameter as the No. 0, but is twice the height, and is, therefore, capable of considerable currents. The curve in Fig. 97 shows the discharge of a No. 00 through 5 ohms, from which it is seen that the life is practically the same as with a No. 0 through 10 ohms. As a matter of

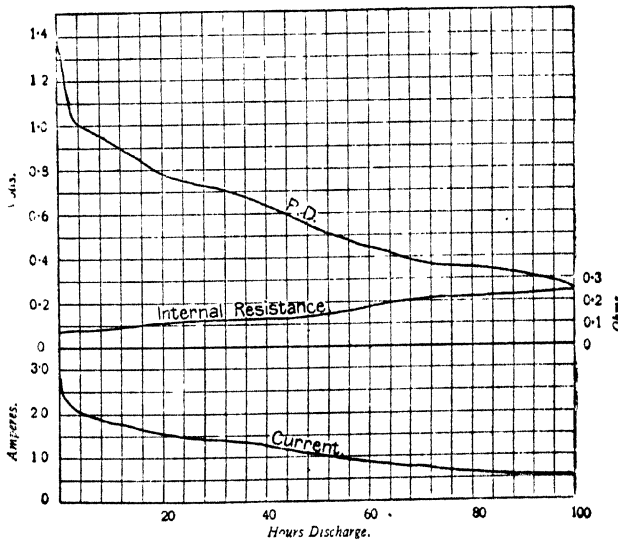


FIG. 98.—Discharge Curves of Siemens No. 0 Sack Cell.
Continuous discharge through half an ohm external resistance.

interest the discharge curve of a No. 0 cell through 0.5 ohm is shown in Fig. 98, though it should be mentioned that this is much too low a resistance on which to use a cell of this size. Nevertheless the current did not fall below 1 ampere until after 46 hours.

Another sack cell is that known as the "Invicta,"

marked by the Sterling Telephone & Electric Co. In this cell the sack is mounted on a carbon rod which projects at the upper end to carry the terminal and also at the lower end, so that the sack does not rest on the bottom of the jar. The lower end of the carbon is paraffined. Glass beads are threaded on the string around the sack, so as to keep the latter from touching the cylindrical zinc with which it is surrounded. The sides of the glass jar near the bottom are indented, giving projections on which the zinc rests, so that it does not touch the bottom of the jar.

COMPARISON OF TYPES OF LECLANCHÉ CELLS.—As regards a general comparison, it may be said that if the modern porous-pot type is taken as the standard, the agglomerate type is distinctly inferior in efficiency, because the manganese peroxide in the agglomerate block cannot be thoroughly utilised, though this form of construction has certain advantages in other directions. On the other hand, the sack form of cell is considerably more efficient than the porous pot. Roughly, the output in ampere-hours for cells by makers of repute may be taken somewhat as follows, some makers showing results above these figures and some below :—

Output in Ampere hours down to 0.75 volt.

---	Porous pot.	Sack form
3-pint size.....	60	110
Quart size.....	30	80
Pint size	12	40

The greater output will be readily seen by reference to the curves given above. The sack form has the further advantage of a considerably lower resistance, something like one-eighth of that of the porous-pot type, and, although it is more expensive in first cost, the output obtained is considerably greater, in proportion, than the cost.

EFFECT OF PHYSICAL QUALITY OF THE MANGANESE PEROXIDE.

—Since depolarisation depends upon the removal of hydrogen by the manganese peroxide, it would be expected that the effectiveness of the peroxide would depend to some extent upon the size of the granules. Wherever a molecule of hydrogen is deposited upon the carbon there should be a particle of peroxide present to cause its oxidation. Indeed, from this point of view, we should expect the most effective arrangement to be a mixture of carbon or graphite (as in the dry cells described later), thus forming a large composite electrode.

The importance of fineness in the peroxide has been demonstrated by an investigation by J. G. Lucas* of the British Post Office. Various types of cell were tested as to their suitability for Post Office work. In this class of work the currents used are generally very small, and consequently the running of cells on a resistance so low as 10 ohms is not a suitable test. The resistance of the signalling apparatus generally varies from 1,000 to 3,000 ohms, and the current required is a small number of milliamperes. Thus, the internal resistance of a cell is usually unimportant. Moreover, the service required is very intermittent. Thus, in England, telephone traffic is most dense between 10 a.m. and 12:30 p.m. and between 2 p.m. and 4 p.m., with about half the traffic on Saturdays and very little on Sundays. Consequently tests were arranged on the basis of constant current for $5\frac{1}{2}$ hours† for five days per week and $2\frac{1}{2}$ hours on the sixth day. The currents used varied from about 5 to 80 milliamperes. In tests of this kind, where it is desired to investigate the effectiveness of depolarisation, care must be taken not to overload a cell. The useful life was considered to be at an end when the E.M.F. observed

* Institution of Post Office Electrical Engineers, December, 1910. J

† A discharge for 5 hours per day has been adopted by the Post Office. The above periods give an average of 5 hours per day.

after the day's discharge had fallen 33 per cent., or when the internal resistance per cell had risen to 3 ohms. The limiting E.M.F. was taken as 0.975 volt, or roughly two-thirds of the initial E.M.F. of 1.5 volts.

Fig. 99 shows a test of this kind on two porous pot cells (run in series) filled with granular manganese peroxide.

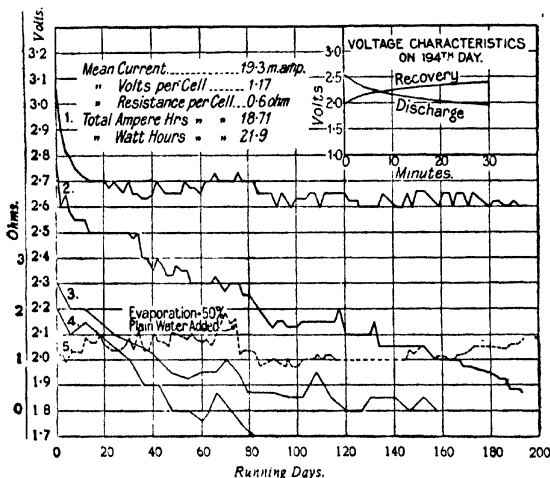


FIG. 99.—Intermittent Test of two 3-pint Porous Pot Leclanché Cells (Granular Manganese Peroxide), at 19.3 milliamperes. (Lucas.)

Curve 1 shows E.M.F. after intervals of rest (*i.e.*, morning readings).
 Curve 2 shows E.M.F. immediately after 5½ hours discharge (*i.e.*, evening readings).
 Curve 3 shows E.M.F. after placing battery on 4-ohm circuit for one minute (after interval of rest, taken on Mondays only).
 Curve 4 is similar to Curve 3, but test was made after period of discharge.
 Curve 5 shows mean daily internal resistance as determined by tests before and after each discharge.

The curves 1, 2, 3, 4 are E.M.F. curves under various conditions, as explained under the diagram, while the other curve shows the value of the internal resistance. The term "Running Days" means the days under test (*i.e.*, excluding Sundays). It will be noticed that the E.M.F. after the daily

rest falls more or less persistently for some time, but then tends to become constant. On the other hand, the E.M.F. after the daily discharge falls persistently. The internal resistance evidently does not vary very much if evaporation is eliminated. In this case the current was 19.3 milliamperes. The small diagram at the right hand top corner shows the fall of E.M.F. during half-an-hour's run on the 194th day of the test, and the corresponding recovery. This test (and those shown in insets in other diagrams) were obtained by discharging the cells on the day following the completion of the main test. For this purpose the cells were placed on circuit and the discharge was interrupted at intervals during the 30 minutes' run to observe the E.M.F.

Fig. 100 shows at X how important it is to adjust the current to the size of the cell. Here the current is 41.6 milliamperes and the life 31 days, with an output of 6.45 ampere-hours; whereas in Fig. 99 the current is 19.3 milliamperes, with a life of about 193 days and an output of 18.71 ampere-hours. The output was therefore increased, as well as the life, by the lower rate of discharge. The characteristics of the discharge and recovery on the 32nd day are seen in the inset on the right-hand side.

If, now, the manganese peroxide is taken out of the porous pot after a life test and is exposed to the atmosphere for two days and is then replaced, a further discharge can be taken; but it is short, as seen by curves at Y in Fig. 100. But if instead of exposing the manganese peroxide to the air it is ground up to powder and replaced, a further discharge may then be taken which is not only longer than that obtained after air exposure, but much longer than the original discharge. This is shown at Z, where the life is seen to be about 218, as against the 31 days originally, with a rather smaller current.

The improvement by the use of powdered manganese peroxide is naturally found to be still greater in the case of

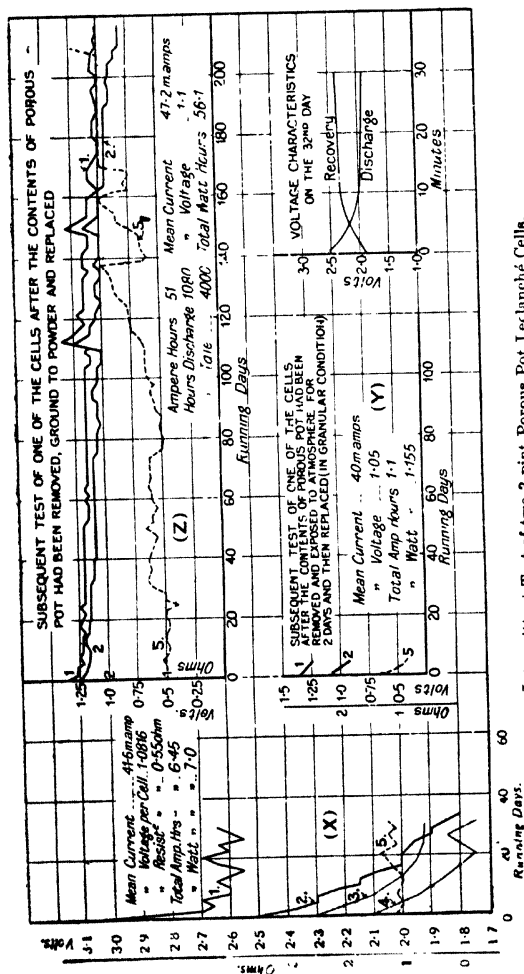


FIG. 100.—Intermittent Test of two 3-pint Porous Pot Leclanché Cells.

(X) Granular Manganese Peroxide.

(Y) Further discharge of one cell after exposing depolariser to the air for two days.

(Z) Further discharge of one cell after powdering the Manganese Peroxide (Lucas)

Curve 1 shows E.M.F. after intervals of rest (i.e. morning readings).

Curve 2 shows E.M.F. immediately after 54 hours' discharge (i.e. evening readings).

Curve 3 shows E.M.F. after placing battery on 4-ohm circuit for one minute (after interval of rest, taken on Mondays only).

Curve 4 shows mean daily internal resistance as determined by test before and after each discharge.

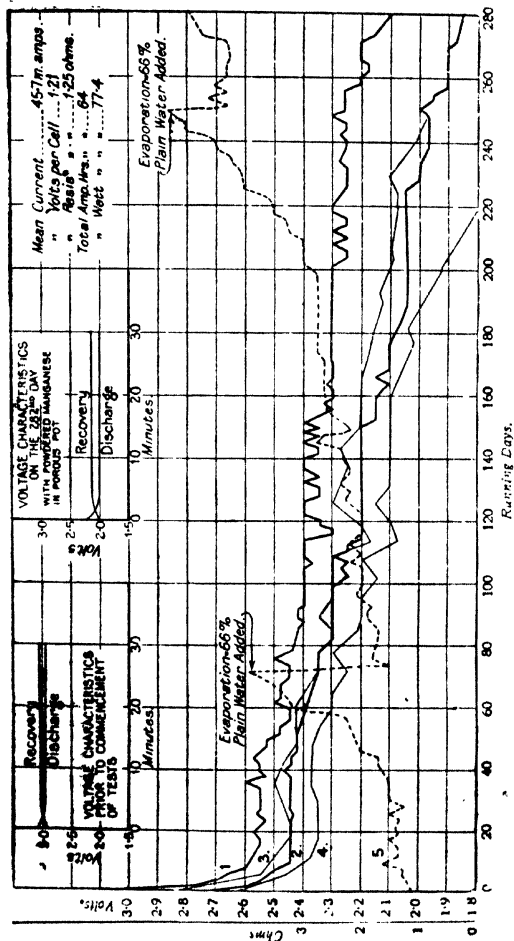


FIG. 101.—Intermittent Test of two 3-jint Porous Pot Leclanché Cells (Powdered Manganese Peroxide) at 45-7 milliamperes. (Lucas.)

Curve 1 shows E.M.F. after intervals of rest (i.e., morning readings).
Curve 2 shows E.M.F. immediately after 5½ hours' discharge (i.e., evening readings).
Curve 3 shows mean daily internal resistance as determined by tests before and after each discharge.
Curve 4 shows E.M.F. after placing battery on 40-hm circuit for one minute (after interval of rest taken on Mondays only).
Curve 5 is similar to Curve 3, but test was made after period of discharge.

a cell that is new, instead of having been subjected to a life test. This is shown by curves in Fig. 101, which should be compared with the curves in Fig. 100. Here the current is 45.7 milliamperes, the life 281 days and the output 64 ampere-hours. With the granular manganese peroxide and a current of 41.6 milliamperes the life was only 31 days and the output only 6.45 ampere-hours. It is noticeable, however, that the variation of internal resistance is much greater with the powdered manganese peroxide, the resistance becoming somewhat high at the end of the test (com-

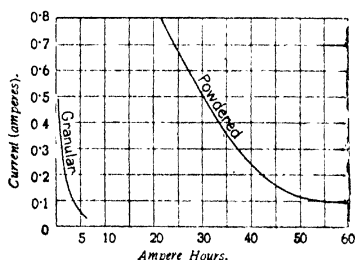


FIG. 102.--Curves showing Ampere-hours obtainable with 33 per cent. fall in voltage on constant current (for various currents) for 5 hours per day 6 days per week. (1) With granulated, (2) with powdered manganese peroxide. (Lucas.)

The Curves apply to 3-pint Porous Cells containing the same weight of materials.

pare Figs. 101 and 99). It has been found that the best results are obtained when the manganese peroxide will pass through a sieve of 50 meshes to the inch, but fails to pass through one of 60 meshes. This fineness, however, would increase the manufacturing cost to a degree which would be commercially impracticable. In fact, in a matter of this kind the course should be taken which gives the best result commercially.

These results are emphasised in a general way by the curves in Fig. 102, which show the ampere-hours

obtainable from porous-pot cells with granulated and powdered manganese peroxide respectively, the weight of material being the same, and the conditions of test being also the same, as outlined above.

As the result of manufacturing, some interesting facts have come to light and have been described by Maurice Solomon in an article on the Leclanché battery in "The Central."* Success does not depend merely on using the right quality of manganese peroxide or in the right proportions. The manganese peroxide is mined in the Caucasus in a form varying from large lumps down to quite small grains. The large lumps, when crushed to grains of about the size of rice, have a crystalline appearance, with sharp edges and corners. On the other hand, small grains found naturally, of the same size, have a rounded appearance without any sharp edges. It is found that if ore of the same quality is taken and of the same sized grain, but the one consisting of crushed grains and the other of rounded grains found naturally, the latter is quite unsuitable for making high-class batteries. It is also necessary to keep the percentage of manganese peroxide and carbon in the mixture within certain very narrow limits, the best results being obtained with about 80 per cent. of manganese peroxide. It is not possible to compensate for a poor quality of manganese peroxide by using a larger proportion in the mixture. As regards the size of grain, the smaller the grains the larger the surface of the peroxide exposed for giving depolarisation. On the other hand, if the grain is very small, good contact is not obtained in loosely packed porous pots; looseness may result through handling in travelling if suitable precautions are not taken, in which case the results are bad. Consequently, for the porous-pot type of cell, Mr. Solomon expressed a preference in the article to which we have referred for grains of the size of rice, but this opinion has

* "The Central," Vol. X, p. 77, 1913.

been somewhat modified towards a smaller size as the result of recent advances.

CELLS FOR POSTAL WORK.—In 1910 (*i.e.*, before the undertaking of the National Telephone Co. was taken over

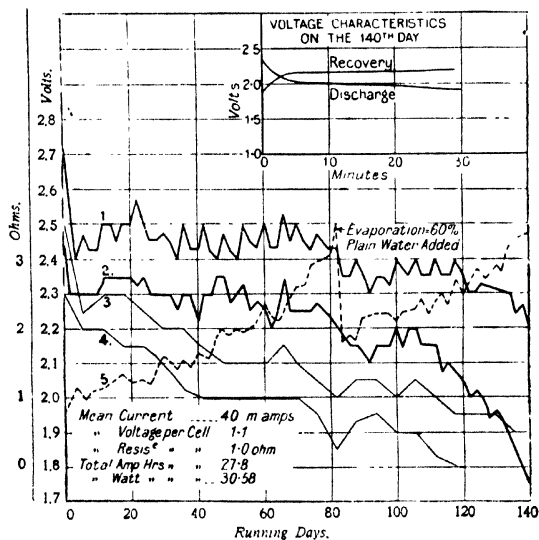


FIG. 103.—Intermittent Test of two 6-block Agglomerate Block Cells, at 40 milliamperes. (Lucas.)

Curve 1 shows E.M.F. after intervals of rest (*i.e.*, morning readings).
 Curve 2 shows E.M.F. immediately after 5½ hours' discharge (*i.e.*, evening readings).
 Curve 3 shows E.M.F. after placing battery on 4-ohm circuit for one minute (after interval of rest, taken on Mondays only).
 Curve 4 is similar to Curve 3, but test was made after period of discharge.
 Curve 5 shows mean daily internal resistance as determined by tests before and after each discharge.

by the Post Office), J. G. Lucas* stated that the British Post Office had in use 105,000 3-pint porous pot Leclanché cells as the standard type for signalling and for miscel-

* *Loc. cit.*

laneous purposes at minor and small exchanges; 43,000 6-block agglomerate block cells, used chiefly for exchange operators' speaking batteries; 29,000 2-block agglomerate cells, used as the speaking battery in subscribers' telephones; 18,600 dry cells (the cases being about 6 in. high by $2\frac{1}{2}$ in. diameter) where wet cells were inconvenient; 11,000 large square dry cells (the cases being about $7\frac{1}{2}$ in. high by 4 in. square); and 26,500 3-pint bichromate cells, generally used at large exchanges. Cells other than of the Leclanché type now form an insignificant proportion of the whole. In 1913 the estimated total number of wet and dry Leclanché cells was 850,000 in use for subscribers' telephones and 250,000 in telegraph offices and telephone exchanges.

Reference has already been made to Post Office tests of porous pot Leclanché cells. Fig. 103 shows a similar test by Mr. Lucas on two 6-block agglomerate cells. The result obtained was very much better than that with the porous pot containing granulated manganese peroxide, but not quite so good as with the powdered peroxide.

Although bichromate cells may be used for supplying small currents (two 3-pint cells gave a life of 100 days on the above basis when giving 21·3 milliamperes intermittently), this class of cell is more suitable for supplying relatively heavy currents, and its output increases as the current becomes larger.

Tests of dry cells will be given in a later chapter.

POST OFFICE SPECIFICATIONS.—The British Post Office makes a practice of manufacturing a certain proportion of the cells required for telegraphic and telephonic purposes, and also purchases large quantities of cells. Consequently specifications are issued for both materials and finished cells as follows:—

Manganese Ore.—To be of such fineness that it will pass through a standard sieve having 40 meshes to 1 in., but to

remain on a standard sieve having 60 meshes to 1 in. To contain not less than 84 per cent. of peroxide, the percentage being determined on a sample which has been dried at 212°F. until the weight is constant. Any loss of weight in drying in excess of $1\frac{1}{2}$ per cent. to be deducted in determining the weight to be paid for.

Ammonium Chloride.—The loss on drying at 212°F. must not exceed 2 per cent. The oxide of iron and other impurities must not exceed 0.15 per cent., and the residue after sublimation must not exceed 0.1 per cent.

Zinc Rods.—The zinc from which the rods are made must not contain more than 0.25 per cent. of iron, not more than 0.5 per cent. of lead, nor more than 1 per cent. total of impurities (excluding mercury). The zinc must be either pressed or rolled to a density of not less than 7.2 at 60°F. There must be thorough amalgamation with pure mercury, and the finished zincs must contain not less than 2.5 per cent. of mercury.

Porous Pots.—To be of China clay, and so fired as to have a resistance not exceeding 0.5 ohm when tested as described below. Dimensions to be as given in the following paragraph. After delivery those pots which are to be tested are prepared by soaking in dilute sulphuric acid (one volume of acid, specific gravity 1.84, to 10 volumes of water) for 72 hours at a temperature of about 60°F. Each pot tested is taken from the soaking trough and placed in the zinc division of a Daniell battery; the pot is then filled to within 2 in. of the top with dilute sulphuric acid as above, the zinc of the battery is placed in the pot, and the resistance is measured by the "half deflection method," first with the pot in position and then again after the pot has been removed.

Porous Cells (i.e., porous pots charged complete).—The porous pot must be in accordance with the preceding para-

graph. The main part of the specification, as issued in in October, 1914, is as follows :—

The dimensions of the porous pot specified in the table below to be strictly followed. The outer dimensions to be in reasonable agreement with the pattern, which will be lent to the contractor for his guidance in manufacture.

Size.	No. 0.	No. 1.	No. 2A.	No. 2A oval.
	Inches.	Inches.	Inches.	Inches.
Internal diameter	4 $\frac{3}{8}$	2 $\frac{3}{8}$	1 $\frac{1}{8}$...
Depth inside	6 $\frac{3}{8}$	6 $\frac{3}{8}$	5	5
Major axis, external (maximum)	2 $\frac{1}{2}$
Minor axis, external (maximum)	1 $\frac{1}{2}$
Maximum overall height of completed porous cells.....	9	9	7	7

The rim of each porous pot to be coated for $\frac{1}{8}$ in. inside and outside with a mixture of ozokerit and pitch, or other specifically approved compound, to prevent creeping.

Each porous cell to contain a carbon rod of suitable size for the cell concerned, the rod to be provided with a metal terminal of approved material and design. The cell to be efficiently sealed and ventilated, but any tube used for the purpose must not project above the sealing compound.

The depolarising mixture of manganese dioxide and carbon surrounding the carbon rod to be in powder form, of high grade quality, and to be well packed. The mixture to be moistened with a dilute solution of hydrochloric acid (strength an ounce of acid to a gallon of water).

E.M.F.—The initial open circuit voltage of a complete cell, consisting of rod zinc in a 15 per cent. (by weight) solution of sal-ammoniac and a porous cell, to be not less than 1.5 volts.

Resistance.—After 12 hours soaking in the sal-ammoniac solution the resistance to be within the limits given in the following table :—

Size of cell.	No. 0.	No. 1.	No. 2A.	No. 2A oval.
Resistance	1 ohm*	1 ohm	1 ohm	1 ohm
Polarisation	15 per cent.	15 per cent.	20 per cent.	20 per cent.

Polarisation.—The polarisation will be ascertained by shunting the cell with 2 ohms for 10 minutes, and then taking the E.M.F. immediately

* Tested with two Zincs, Rod, Leclanché No. 1, for No. 0 cells—one for other cells.

after the shunt circuit is broken. The difference between this voltage and the open circuit voltage, expressed as a percentage of the latter, will be regarded as a measure of the polarisation.

Output.—Of the cells delivered, 2 per cent. drawn at random, will be tested for “electrical behaviour” in a 15 per cent. sal ammoniac solution with a rod zinc (or two in the case of Leclanché No. 0 size) discharging at the current value, as shown in the table below for average periods of five hours per day for six days per week, until the E.M.F. of the cell falls to 0.975 volt. The voltage of the cell will be measured on open circuit immediately after disconnection. The rod zinc and excitant will be renewed as their condition demands during the test.

The minimum output per cell which under these conditions will be considered satisfactory for each of the respective sizes of cell will be as follows :—

Size of cell.	Testing discharge current in milliamperes.	Output (minimum) in watt-hours.
No 0	100	150
No. 1	50	50
No. 2A.....	20	20
No. 2A oval.....	20	20

The cells to be constructed in other respects to the satisfaction of the Engineer-in-Chief to the Post Office or his representative, especially as regards suitability of the cells for six months’ storage without appreciable local action or deterioration. Six cells of the type which the contractor proposes to supply should be submitted with the tender.

In the case of finely powdered mixtures it is desirable to add moisture. This permits the mixture to be rammed down more firmly. Water and weak solutions of ammonium chloride and of hydrochloric acid were tried for this purpose. The last named was found to be the most satisfactory, and it facilitates the absorption of the electrolyte when the cell is set to work.

Figs. 104–106, which have been supplied to the Author by Messrs. Siemens Brothers & Co., show the results obtained on testing Siemens cells made up to the Post Office specification, and tested intermittently as above described.

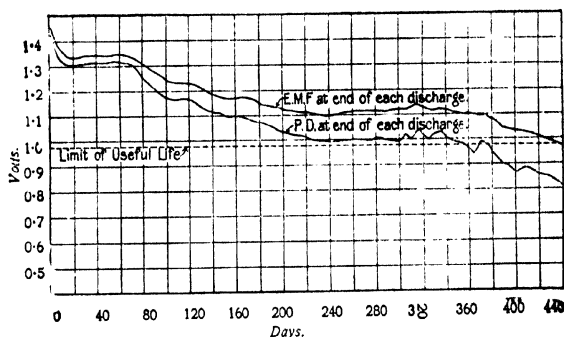


FIG 104.—Discharge Curves of Siemens No. 0 Porous Pot Leclanché Cell, made according to the Post Office specification.

Intermittent test at 100 m.a. for 5 hours per day.

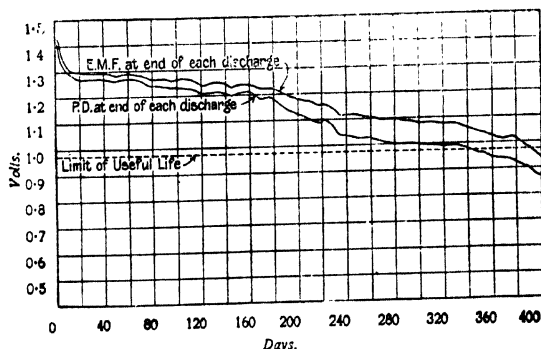


FIG. 105.—Discharge Curves of Siemens No. 1 Porous Pot Leclanché Cell, made according to the Post Office specification.

Intermittent discharge at 50 m.a. for 5 hours per day.

A type of zinc that is sometimes used by the British Post Office is shown in Fig. 107. It is cylindrical in form, and is suspended from the rim of the jar by a hooked projection.

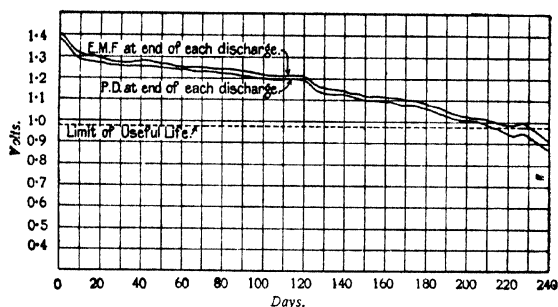


FIG. 106.—Discharge Curves of Siemens No. 2A Porous Pot Leclanché Cell, made according to the Post Office Specification.

Intermittent discharge at 20 m.a. for 5 hours per day.

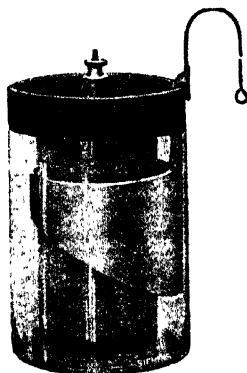


FIG. 107.—Post Office Form of Zinc (in Sack Cell).

The shape is cut so as to give a much reduced surface on the side remote from the suspending hook, it being found that electrolytic solution takes place more on the side where the current is collected.

DETAILS OF LECLANCHÉ CELLS.—When evaporation of a salt takes place in a glass vessel, crystals form on the vessel near the surface of the solution; and since these are maintained more or less moist by capillary attraction of the liquid, the crystals grow upwards and finally grow over the top of the vessel. This “creeping” as it is termed, is avoided in Leclanché cells by dipping the tops of the glass pots into ozokerite or paraffin wax.

The carbon plates are made of retort carbon and were at one time generally provided with a head of lead, cast on



FIG. 108.—Carbon Plate with Lead Cap Corroded by the Electrolyte.

the top, which carried the terminal and made good contact with the carbon plate. It was found, however, that the lead was liable to be attacked by the salt and converted into chloride, rendering it useless. A specimen of this kind is seen in Fig. 108.

The carbon plate and head are now almost invariably made from a single piece of carbon, the terminal being fixed directly into it. Siemens Brothers & Co. simply screw the terminal into the head of the carbon, as seen in Fig. 109, the

top of the carbon being thoroughly paraffined. Or the terminal screw is fixed by running in a readily fusible alloy. Another method, which is employed by Le Carbone for attaching the terminal, is also shown in Fig. 109. It is good both mechanically and electrically, but the lower part is exposed. The terminal screw passes down a vertical hole in the carbon into a slot cut through the head, and is held in position by a nut in the slot and also by a nut above.

It is usual now, instead of cutting plates out of retort carbon, which is expensive, to grind up the carbon, mix it with tar and

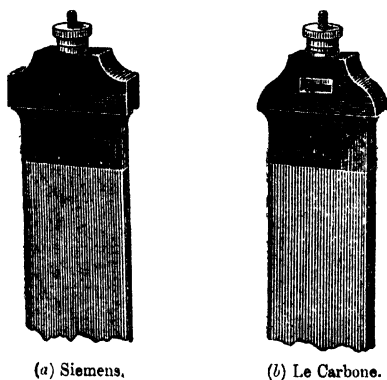


FIG. 109.—Carbon Head and Terminal.

mould it under pressure to the required shape. The carbons so made are slowly brought up to a red heat in retorts, and are maintained at that temperature for some hours.

In order to prevent the capillary attraction of the electrolyte up the carbon plate, and consequent creeping of the salt, the heads are coated with black varnish.

SPECIAL EXCITING SALTS FOR LECLANCHÉ CELLS.

It is often observed that the zinc rod in a Leclanché cell is covered with crystals, and that the rod is

attacked more rapidly near the surface of the electrolyte than anywhere else, with the result that it is liable to drop off before it has been completely utilised. These crystals, which consist of a double chloride of zinc and ammonium, are avoided if the solution is not too strong—for example, 3 oz. to the pint of water. The corrosion at the surface of the solution, however, is not readily avoided, as it is due to the presence of oxygen in the electrolyte and consequent oxidation. There is also a tendency for the zinc to be eaten away in the form of a cone, the smallest amount of corrosion taking place at the bottom. This may be partly due to the solution becoming denser at the bottom of the cell than at the top, owing to the formation of chloride which falls to the bottom. A "concentration cell" is thus formed (*see* p. 119), and local action sets in, the zinc being dissolved where the solution is more dilute, *i.e.*, near the top.

A number of salts are now on the market for which it is claimed that they do not crystallise, and that they cause the zinc to be consumed uniformly. The method of preparation of these salts is a trade secret. An analysis by G. T. Moody of the salt supplied by Leclanché et Cie. gave the following result :*

Zinc chloride.....	20.00
Ammonium chloride	75.81
Moisture given off at 150°C.	2.91
Sodium sulphate	0.48
Moisture given off above 150°C., and impurities	0.8
	<hr/>
	100.00

The tendency to creep was found to be more marked than in the case of ammonium chloride, and the solubility as compared with ammonium chloride was 1.36 : 1. As the salt is not deliquescent it appears to be a mixture of the double chloride, $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl}$, with ammonium chloride.

* Ayrton's "Practical Electricity."

"Salcetron," made by the General Electric Co.; "Siebrosal," by Siemens Brothers & Co.; and "Voltoids," supplied by F. S. Bayley, Clanahan & Co., may also be mentioned.

Beyond a slight improvement in the uniformity with which the zinc is consumed, the Author has not found any great advantages over ammonium chloride in the use of special salts. Their non-deliquescent nature seems rather a matter of degree.

The zincs are generally amalgamated on the surface, but zinc amalgam is sometimes used throughout, as in the "Non-Incrusting Zincs," made by Siemens Brothers & Co., so as to maintain an amalgamated surface, on which incrustation takes place less readily than on zinc alone. Zinc rods are also sometimes made of larger cross-section about the centre than at the ends (for example, by British Insulated & Helsby Cables, Ltd., and by Siemens Brothers & Co.), so as to allow for the greater corrosion that takes place near the surface of the electrolyte.

AMALGAMATED ALUMINIUM.—It has been pointed out by A. J. Paine * that although plain aluminium gives poor results as an electro-positive metal in a cell, its properties are much improved by amalgamation. In fact, amalgamation raises the E.M.F. by about $\frac{1}{2}$ volt. This is an effect which is not easy to understand. Soft aluminium is preferable to that which is hard-rolled.

* *The Electrician*, Vol. LXXII., p. 258, 1913.

CHAPTER IX.

TWO-FLUID CELLS.

Daniell Cell, p. 235 -- Mnott's Cell, p. 239. — Gravity Daniell Cells, p. 241.—Callaud's Gravity Cell, p. 242.—Meidinger's Gravity Cell, p. 243.—Kelvin's Tray Battery, p. 244.—Grove Cell, p. 246.—Bunsen Cell, p. 247.—Two-Fluid Bichromate Cells, p. 250.—Bleek-Love Cell, p. 250.—Decker Cell, p. 255 —Hyposulphite as an Excitant, p. 255.

THE DANIELL CELL.—The principle of this cell and the reactions occurring in it have already been explained in Chapter III., and therefore do not require further discussion.

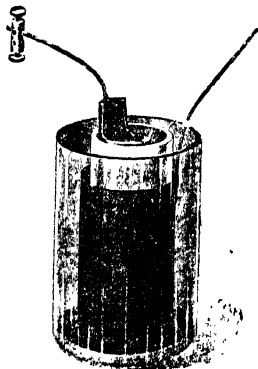


FIG. 110.—Daniell Cell.

The usual form of Daniell cell is shown in Fig. 110. It consists of an outer glass jar containing a porous pot of unglazed earthenware in which is placed the zinc plate or rod. Outside the porous pot is a cylindrical sheet of copper

forming the electro-negative plate. The outer jar is filled with a strong solution of copper sulphate, and the porous pot with dilute sulphuric acid or a solution of zinc sulphate.

The E.M.F. of a Daniell cell varies from about 1.07 to 1.14 volts, the value depending chiefly upon the density of the solutions. The E.M.F. is increased by increasing the density of the copper sulphate, but is diminished by increasing that of the zinc sulphate.

The area of the copper plate is of some importance. The greater the area the more effective is the depolarisation, because there are fewer polarising ions per unit area to be removed in a given time. It therefore follows that the form of cell shown in Fig. 110 is preferable to the older form, in which the size of the copper plate was reduced by placing it inside the porous pot, the zinc plate being outside.

The depolarising action falls off if the copper sulphate solution becomes weakened. For this reason, if the cell is required to give a moderate current for a long time, it is better to fill the outer jar with copper sulphate crystals as well as with solution, the crystals being packed more particularly between the copper plate and the porous pot, as it is in this part that the solution becomes deprived of the copper salt. The objection to placing crystals in this position is that the internal resistance of the cell is increased; but there is a gain in constancy. In some cells, like the one shown in the illustration, the copper plate is made very little larger than the porous pot so as to diminish the internal resistance. In such cells the crystals have to be packed outside the copper plate and, therefore, do not affect the internal resistance, but the strength of the copper sulphate solution is not so well maintained because it must depend to a much larger extent upon diffusion. If, on the other hand, a cell is required to give a heavy current, nothing is gained by adding crystals, because they do not dissolve rapidly enough to be of value; and if placed between the copper plate and the porous pot

they only serve to increase the internal resistance and diminish the available solution.

The effect produced by the addition of crystals is shown by the curves in Fig. 111, which refer to the discharge of quart-size Daniell cells placed on a circuit of a quarter of an ohm. Curve A shows the result obtained when a concentrated solution of copper sulphate is used; curve B refers to the same cell when packed with crystals. The current is seen to be too heavy to remain constant until after it has fallen to half an ampere, and nothing is gained by adding the crystals. The cell in question continued to give about half an ampere for 60 hours. If the current required were only a quarter of an ampere it might be advantageous to add crystals to the solution.

A convenient strength for the sulphuric acid is obtained by mixing one volume of the concentrated acid with 10 volumes of water. In place of sulphuric acid, a solution of zinc sulphate may be employed, and has the advantage that amalgamation is then unnecessary to prevent local action. There is, however, the disadvantage that the internal resistance is higher, but much greater constancy is obtained, and the strength of the zinc sulphate solution may be so chosen that any falling off in E.M.F. due to polarisation is for a long time counterbalanced by the decrease of internal resistance due to the increasing conductivity of the zinc sulphate as the zinc passes into solution. This is shown in Fig. 111, where curve C refers to a cell in which the zinc sulphate solution was made up by dissolving 1lb. in a pint of water; a solution of one-eighth the strength gave a discharge curve similar to C, but about 0.1 ampere below it. There appears to be a further disadvantage in the use of zinc sulphate, viz., the output of the cell is diminished.

In the Daniell cell the porous pot is a source of trouble, as it is in all two-fluid cells. Such a cell cannot be left standing for long periods of disuse, because diffusion takes

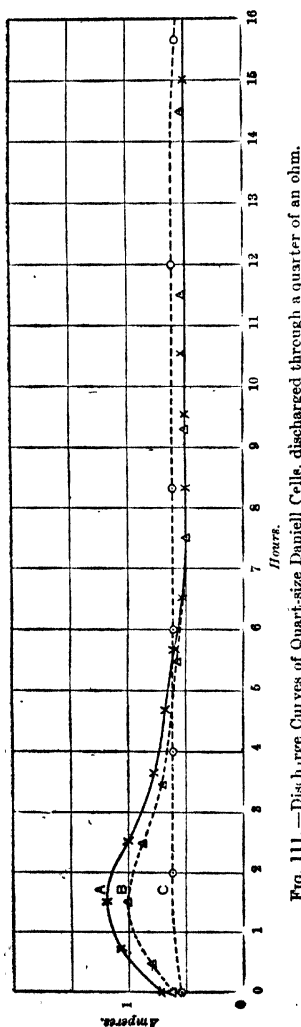


FIG. 111. — Discharge Curves of Quart-size Daniell Cells, discharged through a quarter of an ohm.

place, and the copper sulphate slowly penetrates to the zinc plate on which it deposits the copper either as metal or oxide, giving rise to local action. There is also trouble on account of a transference of the electrolyte, known by the name of electric osmosis, when a cell is giving current. For example, the sulphuric acid (or zinc sulphate) is forced through the pores of the porous pot into the other compartment, even though the level of the electrolyte in the latter may be much higher than that of the sulphuric acid. There is also a risk of porous pots cracking if they are not in use and are allowed to dry, owing to the crystallisation of metallic salts in the pores.

A form of cell which is designed to avoid the diffusion of the copper sulphate, and is due to Siemens and Halske, is shown in Fig. 112. The

porous pot is in the form of a cup with a glass tube cemented into it, as indicated by the dotted lines in the figure. This cup is surrounded by a diaphragm of paper pulp, which supports the positive plate in the form of a ring of zinc. The porous pot is filled with crystals of copper sulphate and water, the outer vessel being charged with dilute sulphuric acid. It is stated that these cells can be used for long periods, the only maintenance that is required being an occasional addition of water to the outer jar to compensate for evaporation. This particular form

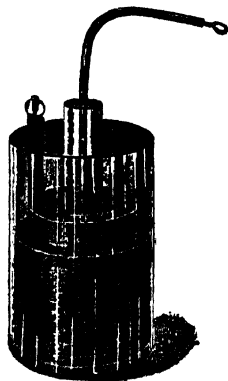


FIG. 112.—Daniell Cell, by Siemens and Halske.

of construction has the disadvantage that the surface of the copper is small, and as the distance between the copper and zinc is considerable, the internal resistance is high viz., from 10 to 15 ohms.

MINOTTO'S CELL.—In Minotto's modification of the Daniell cell the porous pot is replaced by a layer of sand or sawdust, and since any diffusion must take place vertically, trouble due to osmosis is avoided. The copper plate is placed at the bottom of the jar, and has a gutta

percha-covered copper wire, A, attached to it, which forms the positive terminal, as shown in Fig. 113. This insulation guards against accidental contact with the zinc plate and also prevents local action. Upon the copper plate is placed a layer, B, of copper sulphate crystals, and above this, but separated from it by a disc of cloth, is a layer, C, of sand or sawdust. Upon the latter is placed a second piece of cloth or canvas, and finally the disc of zinc⁺D. The cell is set in action by filling the jar with a solution of zinc sulphate, care being taken that this does not reach the brass terminal. If the cell is required for immediate use,

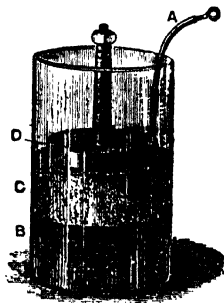


FIG. 113.—Minotto's Cell.

the sand or sawdust should be moistened with zinc sulphate before it is placed in position in the jar; otherwise the solution may take some time to reach the copper plate and to form a continuous circuit. Water is sometimes used instead of zinc sulphate; but, in starting, this gives a very high internal resistance which is diminished only when the copper sulphate diffuses up to the zinc sulphate, zinc sulphate being then formed on account of copper being deposited upon the zinc.

The Minotto cell has a high internal resistance (from 10 to 20 ohms), but, on account of its simplicity and the

small attention which it requires, it is well suited to certain classes of work.

GRAVITY DANIELL CELLS.—If crystals of copper sulphate are placed at the bottom of a beaker of water it will be noticed that the salt diffuses very slowly into the upper layers of the water, being restrained by the force of gravity. Therefore, if the sawdust and cloth partitions were removed from a Minotto cell, we should expect the zinc sulphate solution to be coloured with copper sulphate near the crystals but to remain clear and free from copper sulphate near the zinc. We should then have what is known as a "Gravity Daniell," in which no

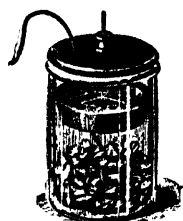


FIG. 114. —Gravity Daniell Cell.

porous pot is used, and the separation is due simply to the density of the copper sulphate. Such a cell is shown in Fig. 114. Connection with the copper plate is made by means of a gutta percha-covered wire, as in the Minotto cell, the plate being covered with a layer of copper sulphate crystals. The zinc is supported by the wooden cover of the jar. The objection to this form of cell is that it is not very portable, because shaking will, of course, increase the diffusion of the copper sulphate. In any case diffusion will take place until the copper sulphate reaches the zinc if the cell is out of use for any length of time; but when the cell is supplying a current the copper is deposited instead of diffusing towards the zinc.

When, therefore, such a cell is **not** in use, it is better to allow it to generate a small current continuously or to dismantle it.

There are many special forms of gravity cell, among which may be mentioned Callaud's cell, Meidinger's cell, Lockwood's cell, and Thomson's (Kelvin's) tray battery, which is largely used in submarine telegraphy. The two former and the last will be described in detail.

CALLAUD'S GRAVITY CELL.—As shown in Fig. 115, the zinc in this cell is in the form of a cylindrical ring, Z, suspended from the rim of the jar by means of three copper

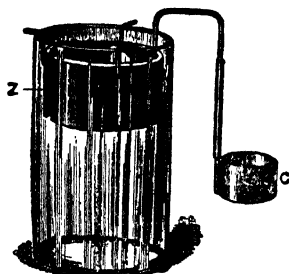


FIG. 115.—Callaud's Gravity Cell.

hooks. The negative plate is a cylindrical ring of sheet copper as seen at C, connection being made by a gutta percha-covered wire. The particular cell of which the illustration is given is intended to be used in series with a number of others. The terminal of the copper plate is therefore riveted and soldered to the zinc ring, the copper ring there shown really forming part of the next cell in the series.

The cell is charged by filling the jar with copper sulphate crystals until the copper plate is covered, and then adding a dilute solution of zinc sulphate until it nearly reaches to the top of the zinc.

MEIDINGER'S GRAVITY CELL.—Various attempts have been made to diminish the diffusion of the copper sulphate in gravity cells and to render them more portable. In Meidinger's cell, of which Fig. 116 is a section, the copper sulphate crystals are contained in an inverted balloon-shaped flask, A, which is closed by a cork through which there passes a glass tube, B. The copper sulphate diffuses through this tube, maintaining the strength of the solution in the neighbourhood of the copper plate C. The terminal wire of the copper plate is insulated with

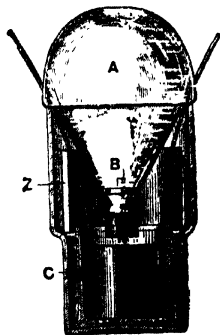


FIG. 116.—Meidinger's Gravity Cell.

gutta percha. The zinc plate Z is of larger diameter than the copper plate, and rests upon an enlargement of the glass jar at a higher level than the copper. The outer jar is charged with a weak solution of magnesium sulphate (one part of the salt to four or five parts of water by weight). The flask is filled with copper sulphate crystals and water, and after the cork and its tube have been inserted, it is placed in position. Since the plates are close together, the internal resistance is comparatively low, varying from 2 to 6 ohms, but the depolarisation is not very effective owing to the small size of the copper plate.

KELVIN'S (THOMSON'S) TRAY BATTERY.—In this battery the solution is contained in a wooden tray lined with lead, and having inclined sides: the size of the tray is generally 18in. square and $4\frac{1}{2}$ in. deep. The lead is brought over the edges and at each corner is carried down under the tray, as shown at L in Fig. 117. A strip of sheet copper, about 1in. in width, is soldered at one end to the centre of the lead lining. In preparing the tray for use, a coating of varnish or paint is applied all over the lead on the inside, so as to prevent it from being acted on voltaically, but the copper strip is left clean. When

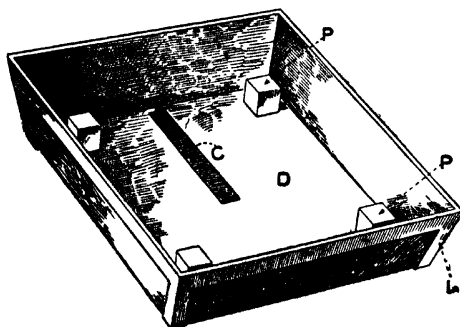


FIG. 117.

dry, a thin copper sheet, varnished on the under side and pierced by a slit in the centre to allow the copper strip to pass through, may be placed in the bottom of the tray, and the copper strip bent down and sprung so that it makes good contact with the plate. The more usual method at present, however, is to spread a sheet of Dutch-metal foil over the bottom while the paint is still wet, the copper strip being brought through and pressed down on to the upper surface, as seen in Fig. 117, where C is copper, D is Dutch metal, and L is lead. In the tray are placed four porcelain supports, P, on which rests the zinc; the latter is seen at Z in Fig. 118, and is in the form of a heavy grid. The

cell is really a gravity cell; but as the space between the plates is small the zinc is protected underneath and round the sides by parchment paper (not shown in the figure) which is tied round it so as to form what amounts to a porous pot separating it from the copper sulphate. It will be noticed that the zinc has upwardly projecting corners, *F*, which rise above the level of the tray. It is thus easy to put a number of trays in series by standing one on top of another, up to ten cells, the lead under the corners of each tray resting on the corners of the zinc of the cell

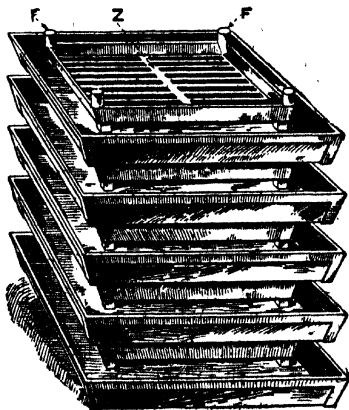


FIG. 118.

beneath. If a copper sheet is used there is a full surface of copper to start with, and the cell will be ready for action if zinc sulphate solution is poured into the parchment cell, and copper sulphate and crystals are placed in the tray. But if Dutch metal is used as above described, the surface of copper is small, and therefore it is usual to fill both compartments to the same level with water, add copper sulphate crystals to the tray, and short-circuit the cell for a night or so. By this means zinc sulphate is gradually formed in the neighbourhood of the zinc and copper in

deposited over the surface of the Dutch metal. When the cell is in circuit, there is a continual deposition of copper; but if the sheet becomes inconveniently thick it is easily stripped from the lead owing to the layer of paint separating this from the Dutch-metal. When the battery is in use some of the zinc sulphate solution should be removed daily and be replaced by water so that the specific gravity is kept at about 1.24: this should not be less than 1.12, nor greater than 1.3. If the zinc sulphate is not kept sufficiently dilute, crystals accumulate round the edge. The strength of the copper sulphate should be maintained by adding crystals from time to time. When a battery is not in use it should be allowed to generate sufficient current to prevent diffusion of the copper sulphate to the zinc.

Owing to the construction of this battery, the internal resistance is low. At one time it was largely used for working syphon recorders, but it has now been generally superseded by accumulators, which have the advantage of lower internal resistance and give less trouble.

THE GROVE CELL.—The depolarisation in this cell, as already explained in Chapter III., depends upon the oxidising power of nitric acid. A very usual form of Grove cell is shown in Fig. 119. The outer jar is rectangular in shape, and contains a zinc plate, Z, in the form of a U, the space between the upright parts being sufficient to allow a narrow porous pot, P, containing the platinum sheet (not shown in the figure) and nitric acid to be placed between them. The outer jar is filled with dilute sulphuric acid. A very compact form of cell is obtained by this construction. The E.M.F. varies from 1.9 to 2 volts. Since the internal resistance is low and the depolarisation is good, relatively large currents can be generated. In Fig. 121, the discharge curve marked A was obtained from a cell of this description, the size of the outer jar being 4½ in. by 2½ in. and 5½ in. high. The form of zinc used in the cell described above is good as regards diminution of internal resistance, but it is

inconvenient for amalgamation, because the inner parts are not very accessible. On that account a cylindrical form of cell is preferable. For the sake of ease in re-amalgamating, zincs should always be made as open as possible. For the same reason the zinc used in the cell shown in Fig. 110 is not very suitable, because it is made in the form of a hollow cylinder of small diameter, the interior of which is not easily cleaned.

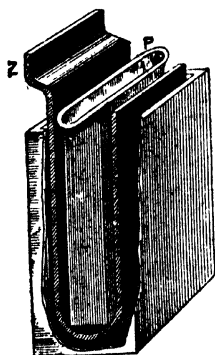


FIG. 119.—Grove Cell.

An objection to the use of nitric acid as a depolariser arises from the fact that its reduction results in objectionable corrosive fumes owing to evolution of nitric oxide, which oxidises in the air to the red nitrogen peroxide. Such cells should therefore be worked in positions where the fumes are easily carried away, and not in closed rooms.

THE BUNSEN CELL—This cell is the same as the Grove cell, except that carbon is used in place of platinum. The construction, however, is somewhat different to that of the Grove cell which has just been described, because carbons are more easily made in the form of rods and are, of course, more bulky than the platinum sheet. A common

form is illustrated in Fig. 120. Here the zinc is cylindrical and is amalgamated without much difficulty on the inside, where the corrosion takes place.

The porous pot in a cell of this kind should be as large as possible, because the capacity depends chiefly upon the power of depolarisation—that is, upon the amount of nitric acid. The use of carbon in place of platinum is not attended with any appreciable disadvantage, as the E.M.F. is practically the same, and there is, of course, the advantage that the cell is much cheaper in first cost.

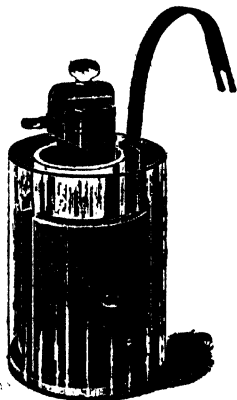


FIG. 120.—Bunsen Cell.

In the usual form of cell, however, there is trouble from corrosion of connections; and carbons do not last indefinitely like platinum, which apparently does not deteriorate if it is occasionally heated to dull redness to prevent it from becoming brittle.

In Fig. 121 is given a discharge curve, B, obtained from a quart-size Bunsen cell discharging through a circuit of half an ohm. The curve obtained by substituting platinum for the carbon (giving a Grove cell), with the same

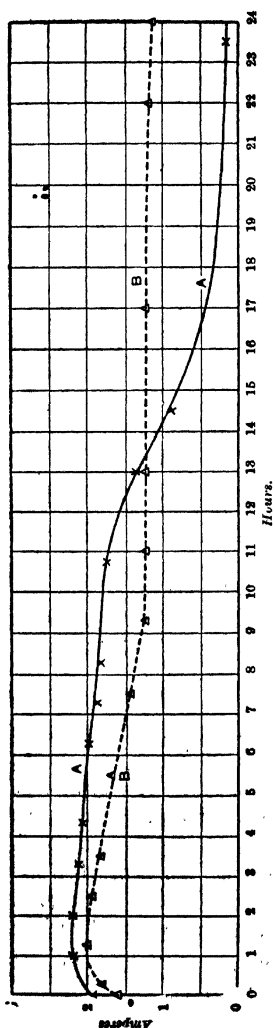


Fig. 121. — Discharge Curves of Grove and Bunsen Cells, discharged through half an ohm.

quantity of nitric acid, is very similar. It will be noticed, by comparison with the curves in Fig. 111, that a Bunsen cell is capable of giving a much heavier discharge than a Daniell cell of equal size, and it has the further advantage that the E.M.F. is almost twice as great. On that account the resistance used in obtaining the curves in Fig. 121 was made double that employed for the discharges in Fig. 111 in order that the results might be more comparable, one Bunsen cell being roughly equivalent to two Daniell cells in series.

A number of modifications have been suggested in order to avoid the objectionable fumes arising from the nitric acid. The substitution of a nitrate for the acid renders the cell useless, as the depolarisation is very feeble. A mixture of a nitrate and sulphuric acid is some-

times recommended; but the E.M.F. is much reduced and the discharge is unsatisfactory if a heavy current is required. J. W. Swan* has proposed the following non-fuming solution as giving a result nearly equal to that of nitric acid :—

Nitric Acid (density 1.42).....	1 part by weight	
Chromic Acid	3 parts	„
Sulphuric Acid	6 „	„
Water.....	5 „	„

According to the Author's experience the above quantity of chromic acid is more than can be held in solution.

Iron has also been suggested as a substitute for platinum in the Grove cell, or for the carbon in the Bunsen cell. Owing to the passive state which it assumes when placed in concentrated nitric acid it does not dissolve, but since it is attacked with evolution of corrosive fumes when the acid becomes weak, it is not very suitable for the purpose.

TWO-FLUID BICHROMATE CELLS.—These cells were discussed in Chapter VIII. in connection with one-fluid bichromate cells, and therefore do not require further notice in the present chapter; but some special two-fluid cells have been developed in which bichromate enters as the depolariser, and two of these are described in the following pages.

THE BLEECK-LOVE CELL.—This cell, which is due to Mr. W. A. F. Bleeck, of Brisbane, and Prof. T. R. Lyle, of Melbourne, is of more than usual interest because its E.M.F. is higher than that of any other primary cell, except the zinc/lead-peroxide type. The construction is shown in Figs. 122 and 123. A cylindrical carbon, C, is suspended in a glass jar by a carbon ring, A. This ring also carries a cylindrical porous pot, P, which is provided with a wooden cover, B, carrying a cylindrical zinc, Z. The

* B. A. Report, 1889, p. 512

porous pot is glazed down to a point, D, but is porous below that level, and is, of course, closed at the bottom. The

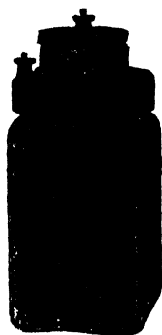


FIG. 122.—Bleek-Love Primary Cell.

electrolyte consists of a chromic acid depolarising solution in the glass jar and a caustic soda excitant solution in the porous pot, and it will be noticed that the level of the latter

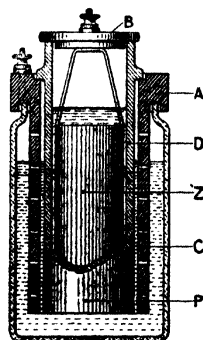


FIG. 123.—Section of Bleek-Love Cell.

stands at a considerably higher level than the chromic solution. The acid solution is sold already prepared along

with tins of caustic "crystals" for making up the alkaline solution to the required strength.

According to the patent specification* the depolarising liquid consists of a mixture of hydrochloric and chromic acids with ferrous or nickel sulphate, or both. It may be prepared by taking the following proportions:—

Hydrochloric acid (commercial)	5 fluid oz.
Water	15 oz.
Ferrous or nickelous sulphate	1 oz.
Chromic acid (commercial, added to the above solution)	8 oz.

The excitant is made by adding 1 oz. of gum arabic solution of 1·12 sp. gr. to 10 oz. of water and then adding 5 oz. of commercial caustic soda. The object of the gum arabic is to retard the diffusion of the excitant through the porous pot.

The E.M.F. is about 2·5 volts, and this high value is due to the fact that the cell is a Becquerel cell with zinc instead of a neutral element for the electro-positive plate.

The question naturally arises whether the E.M.F. of the Becquerel portion of the combination will be maintained when the cell is in use. Experiment shows that this part of the E.M.F. is maintained for a long period. The caustic soda being at the higher level there is a slow flow into the bichromate department. On the other hand, it is noticeable that some bichromate finds its way into the caustic solution and is reduced by the zinc, giving rise to the familiar green colour due to reduction within the porous pot.

Upon replacing the zinc by a carbon plate it is found that the E.M.F. due to the junction of the two solutions is 0·85 volt when the cell is first set up. What may, therefore, be regarded as the true voltaic part of the E.M.F. amounts to 1·65 volts.

Some tests made by the author upon a cell having a glass jar 6½ in. high by 4½ in. square gave results shown

* British Patents, Nos. 5,297 of 1908 and 15,194 of 1909.

in Fig. 124. Curve A shows the discharge through a resistance of about 0.97 ohm. There is a considerable drop in the current during the first three hours, from which it would seem that this size is better suited to a lower discharge rate if a reasonably constant current is desired. For this reason another discharge was run with a new porous pot, the external resistance being raised to about 1.4 ohms. Curve B

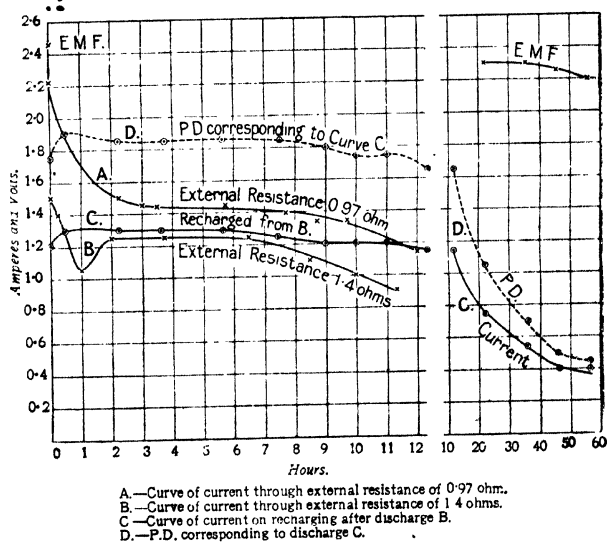


FIG. 124.—Discharge Curves of Bleek-Love Cell on constant external resistance.

shows the result, the current being steadier. At the end of the discharge the porous pot was put to soak in water for the night and the cell was recharged the next morning. The resulting discharge on the same resistance, as seen by Curve C, was much more steady. The cell was then left on circuit for $2\frac{1}{2}$ days, during which time the current and P.D. fell as shown in the right-hand part of the diagram. It was

noticeable that the E.M.F. immediately on opening circuit always showed a high value, as seen by the curve for E.M.F. It must, therefore, be concluded that the fall in current is not due to polarisation (contrary to what might be anticipated, as it might be thought that the Becquerel part of the E.M.F. would fall off), but to increasing internal resistance. The porous pots, the porosity of which is very fine, appear to increase rapidly in resistance, and a more constant result is obtained after this increase has taken place. Soaking the porous pot in water after discharge reduces the resistance to some extent, and when a little time has been given for the absorbed water to be displaced by the solutions a fairly constant discharge is obtained for some hours, as shown by Curve C. It is noticeable that the bichromate is not in an exhausted condition at the end of a prolonged discharge, such as that here described.

The cell appears to have been used to some extent in Australia in small central battery exchanges for telephonic work and for purposes where other sources of electrical energy were not available. For giving considerable constant currents for short periods the cell does not seem so suited as some of the simpler varieties of primary cell. Also the porous pot requires careful soaking after use owing to the presence of caustic solutions, and on this account dilute sulphuric acid would probably be preferable to water for the elimination of the caustic soda after some preliminary washing. The resulting salt in the pores could then be washed out fairly easily by further soaking. On the other hand, the use of a caustic solution is an advantage in preventing local action, which is an invariable trouble with acid electrolytes, more particularly with bichromate, because reduction of the depolariser is a necessary accompaniment of local action, and there is, therefore, a double loss.

A similar type of cell, using nitric acid and caustic soda, was described by E. G. P. Bousfield* in 1904.

* "The Electro-Chemist," Vol. 3, p. 730, 1904.

THE DECKER CELL.—This cell, which is due to F. A. Decker, of Philadelphia (U.S.A.), has been described by F. B. Crocker.* The electrolyte consists of dilute sulphuric acid in porous pots containing zinc plates, and a mixture of sodium bichromate and sulphuric acid surrounding the porous pots, the other plates being carbon. The special features of the cell are concerned with the porous pots and carbon plates and with the manipulation of the electrolytes. The porous pots are built up from earthenware plates, having ribs on one side to strengthen them and thickened edges. These plates are united to form a flat cup, the ribs being inside, and are then ground down until they are so thin that the light shows through them. Thus a porous pot is obtained of which the sides are much thinner than would be otherwise possible, and the internal resistance is correspondingly reduced. The electro-negative plates are of graphite, corrugated so as to oppose a large surface to the depolariser and strengthened at the edges. The containing vessel is made of vulcanite, and beneath the vessel are two ducts. One of these makes connection to each of the porous pots, there being as many branches as there are porous pots. The other duct has one branch to each cell. By connecting the two ducts to reservoirs containing the acid and the depolariser respectively, a battery of cells can be charged by raising the reservoirs. The branch ducts are made small so as to avoid local currents from cell to cell.

The Author is not aware whether this cell is still on the market.

HYPOSULPHITE AS AN EXCITANT.—The use of sodium hyposulphite as an excitant has been advocated by A. J. Paine.† This is used with the zinc in one compart-

* *Transactions, American Electrochemical Society*, Vol. X., p. 107, 1906. Abstract in *The Electrician*, Vol. LVIII., p. 296, 1906.

† *The Electrician*, Vol. LXXI., p. 269, 1913.

ment of a two fluid cell, being separated by a porous pot from the carbon, which is immersed in ferric chloride. From a brief trial the Author has not found any particular advantage in this cell. As a depolariser a ferric chloride solution can easily be maintained saturated by adding the solid, but this solution is a material which is distinctly "messy" when in due time it is oxidised to the form of rust.

CHAPTER X.

DRY CELLS.

General Description, p. 258.—Materials, p. 267.—Obach Cell, p. 268.—Hellesen Cell, p. 272.—E.C.C. Cell, p. 273.—G.E.C. Cell, p. 274.—Dania Cell, p. 276.—Manchester Cell, p. 277.—E.S. Cell, p. 277.—Lessing Cell, p. 278.—Le Carbone (Hudson) Cell, p. 280.—R. & R. Cell, p. 281.—Blue Bell Cell, p. 283.—Columbia Cell, p. 284.—Jove Cell, p. 285.—Mascot Cell, p. 286.—Desiccated Cells, p. 286.—Extra Sec Cell, p. 287.—Dura Cell, p. 288.—H.2.O. Cell, p. 289.—Reliable Cell, p. 290.—W.O. Cell, p. 291.—Burn-Boston Cell, p. 292.—Comparison of Wet and Dry Cells, p. 294.—Testing Dry Cells, p. 297.—Tests to Determine the Condition of a Cell before Use, p. 298.—Life Tests, p. 301.—Standard Methods of Testing Dry Cells, p. 303.—Construction and Tests Specified by the British Post Office, p. 309.—Cells for Laboratory Use, p. 311.—Bibliography, p. 315.

Owing to the want of portability of cells containing liquid electrolytes, there have been numerous attempts to utilise some form of more or less solid electrolyte and thus to produce what is termed a dry cell. That term, however, is really a misnomer. No cell can furnish more than a minute current if it is dry, and; in fact, one of the difficulties experienced in making a successful dry cell is the difficulty of keeping it sufficiently wet under all conditions (such as hot climates). The name is nevertheless a useful one, and is now universally used to designate a class of cell which is relatively dry as compared with the cells which have so far been described.

In addition to portability, dry cells have the further advantages that they require no attention during working,

such as the addition of water, that they are generally unbreakable, and may be used in any position. But certain defects are frequently observed. Deterioration takes place if cells are kept in stock, even if no current is taken from them, and is shown chiefly by loss of E.M.F. and increase of internal resistance. The latter is partly due to the gradual drying of the paste and partly to changes in the salts and other constituents of the cell. If the cells are good they will retain their qualities without serious change for eighteen months, or even two years. Another defect frequently met with in cells which are constructed so that gases generated have no ready means of escape is that known as "bursting," the gases breaking open the outer case. This bursting generally takes place in cells which are on circuit, but it is also liable to occur in cells which have never been used, owing to the gradual expansion which often seems to accompany the drying of the paste. Drying may also be due to the formation of hydrated crystals.

All dry cells at present on the market are practically Leclanché cells in which the electrolyte is in the form of a paste, and consequently the value of the E.M.F. is about 1.5 volts. The exact composition of the paste is generally a trade secret. Depolarisation is usually effected by having a paste of manganese peroxide, carbon and graphite in the immediate neighbourhood of the carbon plate. Instead of peroxide paste, agglomerate blocks and Leclanché-Barbier agglomerate cylinders have also been used by Leclanché et Cie. in dry cells, but without any very great success.

GENERAL DESCRIPTION OF DRY CELLS.—Before going on to a detailed description of certain cells it may be well to state in general terms the construction that is usually adopted.

The container, which is round or rectangular in form to suit the conditions of the user, is made of sheet zinc and forms the electro-positive element. This has the advantage that a water-tight vessel is obtained, this vessel being protected mechanically by a pasteboard casing. Sometimes an earthenware or glass container is used, a sheet of zinc in cylindrical form being placed within the container. The only advantage of this method seems to be that the insulation is better, which may be desirable if a larger number of cells are required in series.

The zinc is sometimes amalgamated. From the point of view of local action this does not seem to be important, but amalgamation appears to prevent the forming of crystals and consequent pitting of the zinc.

The carbon may be a plate or it may be round. It is surrounded by a paste made up of manganese peroxide and carbon, with some graphite to decrease the internal resistance, and electrolytic constituents and water. The proportion of graphite is regulated partly by the cost and depends also on skill in manufacture. The exact composition is not disclosed by makers and depends upon the service required, but it is stated that an average mixture is made by taking—

Manganese peroxide	10 lb.
Carbon or graphite, or both	10 lb.
Sal-ammoniac	2 lb.
Zinc chloride	1 lb.

Sufficient water is added to this mixture to make it into a suitable paste.

A formula given by H. K. Richardson* as being commonly used in the United States is as follows, expressed in parts, presumably by weight :—

Manganese peroxide (85 per cent. MnO_2)	100
Ground coke	80
Artificial graphite	20
Sal-ammoniac	20
Zinc chloride (30°Bé)	7

* "Metallurgical and Chemical Engineering," Vol. X., p. 531, 1912.

The carbon and the depolarising paste surrounding it must be regarded as a composite electrode. The depolarising action takes place at the outer surface of the paste and progresses inwards as the cell is discharged.

Between the depolarising paste and the zinc is what may be called the "electrolytic paste." It is generally white, and is made up of flour,* plaster-of-paris, sal-ammoniac and zinc chloride, with enough water to form a paste. Dextrine and cornflour are also employed. Sometimes a transparent gelatinous paste is used. In this case the electrolyte is made up with gum tragacanth, gelatine or agar-agar. Tragacanth is the best gum for the purpose. Gelatine results in higher resistance; agar-agar is largely used, and has the merit of cheapness.

The usual procedure in manufacture is to make the electro-negative element by ramming the depolarising mixture into a mould round the carbon. For this purpose the mixture is moistened with water, or, if it is desired to obtain greater coherence, with water containing a little mucilage. The carbon and the surrounding depolariser is then removed from the mould, and may be made up into a sack element by wrapping it in canvas which is securely tied round. The advantage of this form of construction is that good contact is secured between the carbon and the depolariser. The electro-negative element is then placed in the container, into which the required quantity of electrolytic paste has already been poured, or the paste may be poured in after the element is in position. When first made, the white paste is sufficiently liquid to pour easily, and sets more or less stiff after one to three hours, according to its composition, the setting being due to the plaster-of-paris.

* In regard to substitutes for flour, see a note in *The Electrician*, Vol. LXXV., p. 375, 1915. Glasswool, sawdust, gelatine, starch, Kieselguhr and water glass are mentioned.

Provided the electrolyte is sufficient there is no advantage in having a thick layer of electrolytic paste. In fact, in American cells this is cut down so far as to consist merely of a few layers of pulp board or blotting paper moistened with the electrolyte. It must be remembered that the depolarising paste also contains electrolyte and this will diffuse as the other becomes used up. An advantage of the blotting-paper method is that the container can be easily lined therewith; the paper is soaked by running in electrolyte, which is poured out again after a few moments; the carbon can then be placed in position and the depolarising paste can be rammed in so as to obtain good contact. Except in America, however, this method has not found favour, although it is cheap. It gives low internal resistance, and therefore a high value of the short-circuit current initially; but such cells tend to dry up more quickly than those made with a paste, the amount of moisture held by the paper being comparatively small.

According to Richardson,* paper for this purpose generally consists of 75 per cent. ground wood pulp and 25 per cent. sulphite fibre, the thickness being 0.040 in. It must be highly absorbent so as to take up enough electrolyte, but the pores must be so fine that the carbon and graphite particles cannot migrate through them under the influence of electro-capillary forces.

Some means must be adopted of preventing the carbon and the depolarising paste from touching the bottom of the zinc container.

Judging from the Leclanché cell, it might be thought that sal-ammoniac would be all that would be necessary for the electrolyte. It appears, however, that zinc chloride minimises local action, and it also, no doubt, keeps the cell from drying up. To prevent the latter, the cell is always finished off with a bituminous or other seal. Further, if zinc

* *Loc. cit.*

chloride is in excess, the ammonia gas due to the action of the cell is converted into ammonium chloride, and does not cause trouble through forcing an exit; moreover, the E.M.F. is maintained at a higher value if the ammonia is removed. On the other hand, insoluble zinc hydroxide is thus formed which is harmful from the point of view of internal resistance.

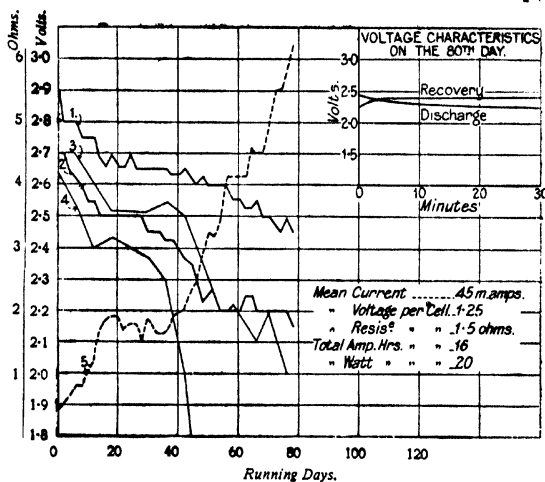


FIG. 125.—Post Office Test of Two Dry Cells in Series. (Lucas.)

Discharge at 45 m.a. for 5 hours (average) per day.

(5½ hours on five days a week and 2½ hours on Saturdays.)

Curve 1 shows E.M.F. after intervals of rest (i.e., morning readings).

Curve 2 shows E.M.F. immediately after 5½ hours' discharge (i.e., evening readings).

Curve 3 shows E.M.F. after placing battery on 4-ohm circuit for one minute (after interval of rest, taken on Mondays only).

Curve 4 is similar to curve 3, but test was made after period of discharge.

Curve 5 shows mean daily internal resistance as determined by tests before and after each discharge.

Since the cell in action gives rise to ammonia it is desirable to provide some means by which this gas may escape, and for this reason a vent tube is generally provided. And objection to this has been pointed out by J. G. Lucas,

namely, that the escaping gas carries moisture with it; thus the cell dries up and the internal resistance increases.* Mr. Lucas carried out intermittent tests at constant current (on the lines already described in Chapter VIII. when dealing with Leclanché cells). Fig. 125 shows the results ob-

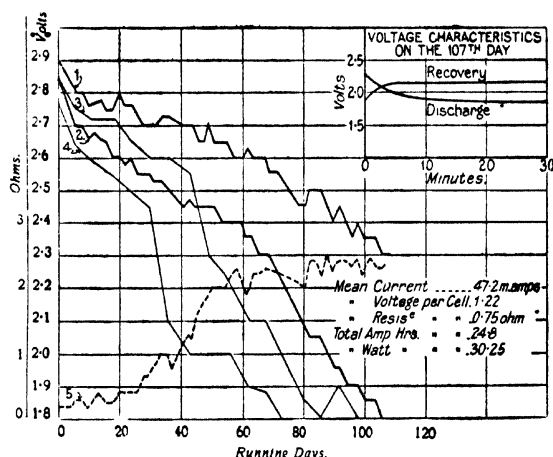


FIG. 126.—Post Office Test of Two Dry Cells in Series provided with a Sealed Expansion Chamber. (Lucas.) Compare with Fig 125.

Discharge at 47.2 m.a. for 5 hours (average) per day.

(5½ hours on five days a week and 2½ hours on Saturdays.)

Curve 1 shows E.M.F. after intervals of rest (*i.e.*, morning readings).

Curve 2 shows E.M.F. immediately after 5½ hours' discharge (*i.e.*, evening readings).

Curve 3 shows E.M.F. after placing battery on 4-ohm circuit for one minute (after interval of rest, taken on Mondays only).

Curve 4 is similar to curve 3, but test was made after period of discharge.

Curve 5 shows mean daily internal resistance as determined by tests before and after each discharge.

tained with cells as supplied by the manufacturer and provided with a vent. Cells of the same kind were then taken and a rubber expansion chamber was fitted to each cell so that the gas could pass into the chamber but could not pass

* *Proceedings, Institution of Post Office Electrical Engineers, 1910.*

right away. The results with the modified cells are shown in Fig. 126. It will be noticed that the internal resistance, instead of reaching a high value, ceases to rise after a time.

In both these diagrams curve 1 shows the E.M.F. just before the daily run and curve 2 shows the E.M.F. immediately after the run. Curve 3 gives the E.M.F. immediately after putting the cells on a 4-ohm circuit for one minute after the interval of rest, and curve 4 the corresponding figure after the daily run. The dotted curve shows the internal resistance. "Running days" means the days under test (*i.e.*, Sundays are excluded).

If the ingredients of the depolarising paste are very fine the gas may have difficulty in escaping and the cell may burst. The fact that a cell has burst is indicated, if not otherwise evident, by a rapid rise of internal resistance.

For small discharges with long intervals (such as may be required in Post Office work) the rise of internal resistance is a serious objection to some types of dry cell. This is illustrated by Fig. 127, which is also due to Mr. Lucas. It will be seen that after 150 days the internal resistance began to rise rapidly and was also considerably higher after each day's discharge than before the discharge, giving rise to two curves. From this it would seem either that diffusion occurred with difficulty after a time, or that gas was formed during the day and was dissipated during the night.

The rise in internal resistance is a troublesome feature of dry cells. It is not due simply to the drying out of a cell. In fact, this is probably only a minor cause, since the voltaic action of the cell itself gives rise to water. It is more probably due to the formation of insoluble double chlorides and basic chlorides which take up water in their formation and which restrict the available path for the current. It is noticeable, however, that the current from an old cell often rises for a time when the cell is placed on circuit, showing that the internal resistance is reduced by

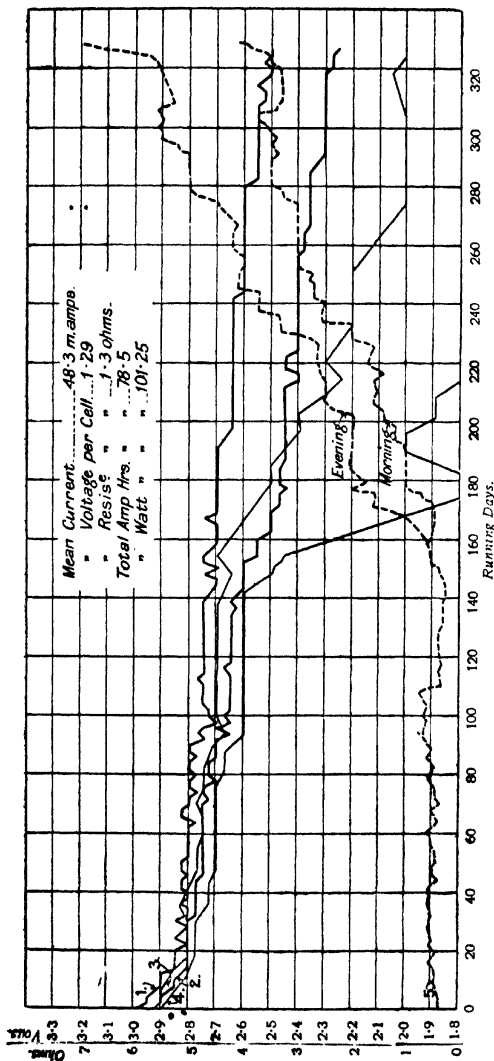


FIG. 127.—Illustrating the Undesirability of having a Large Dry Cell for a Small Current, and the Rapid Rise in Internal Resistance after a Certain Period. (Lucas.)

Discharge at 48.3 m.a. for 5 hours (average) per day.

(5) hours on five days a week and 24 hours on Saturdays.

Curve 1 shows E.M.F. after intervals of rest (i.e., morning readings).

Curve 2 shows E.M.F. immediately after 54 hours discharge (i.e., evening readings).

Curve 3 shows E.M.F. during plating battery on 400-ohm circuit for one minute (after interval of rest, taken on Mondays only).

Curve 4 is similar to curve 3, but taken immediately after each discharge.

Curve 5 shows mean daily internal resistance as determined by test before and after each discharge.

the water that is liberated. Another feature of ageing is the lowering of the E.M.F.

From the point of view of cost of operation the rise of internal resistance may be important because it may set a limit to the life of the cell. Thus, referring to Figs. 125 and 126, Mr. Lucas computes the inclusive cost per watt-hour for Post Office work in the case of the cell whose internal resistance rises rapidly as being 0.6d., whereas the cost for the cell whose internal resistance rises slowly is only 0.37d. These figures are an estimate of the total cost involved so long as the battery remains in use, and includes interest on capital, establishment charges, freight and handling, labour,



FIG. 128.—Fahnestock Terminal.



FIG. 129.—Patterson Screw Top for Dry Cell.

supervision, travelling, materials and estimated value to cover the physical deterioration of permanent parts, if any.

Except for the vent tube, dry cells are always hermetically sealed by means of a bituminous or resinous seal.

The carbon terminal is usually one of the varieties used in Leclanché cells. The zinc terminal is generally a wire, but American makers prefer an acorn-head post soldered to the zinc container, as illustrated in some of the sections of cells on a later page. To facilitate connecting up cells, special devices are sometimes used, such as the Fahnestock connector, supplied by the National Carbon Co. (U.S.A.), and illustrated in Fig. 128. Another American device is the Patterson connection, shown in Fig. 129. The top of the

cell is provided with a screw thread so that it will screw into a large Edison socket. In the case of a battery, a number of these sockets are wired together and it is only necessary to screw the cells home to secure connection. Ignition batteries are conveniently fitted up in boxes in this way. Cabinet outfits are made up on this plan to give up to 150 amperes at a low voltage.

MATERIALS.—What has been said on this subject in connection with Leclanché cells applies largely to dry cells. The manganese peroxide (mainly from the Caucasus or Japan) usually contains 85 per cent. of MnO_2 . The carbon that is used is retort carbon, coke, petroleum coke and other varieties of various qualities freed from iron by magnetic separation. Graphite may be natural or artificial (mostly that known as Acheson B2), but more usually the best qualities of natural graphite, such as that from Ceylon, is employed.

Both the sal ammoniac and zinc chloride must be free from impurities, particularly from iron, otherwise local action results. Local action also occurs if copper passes into solution, since it then becomes deposited on the zinc; in fact, copper is the most harmful impurity in this respect. It might be thought that local action would also occur on account of the solder, but since lead and tin, the constituent metals, have high "over voltages" (*i.e.*; they require considerably more than the P.D. due to the decomposition of water to liberate hydrogen), such action does not take place. Some local action may also arise if the carbon and the depolarising mixture are both in contact with a thin layer of the electrolyte paste, the zinc being on the other side of this layer. Messrs. C. F. Burgess and C. Hambuechen* state that the P.D. between the carbon and the mixture is 0.176 volt.* Consequently it is better to surround the

* *Transactions, American Electrochem. Soc.* Vol. XVI., p. 97, 1909.

bottom of the carbon with the mixture if the zinc is sufficiently near to form part of the path carrying the resulting current.

THE OBACH CELL.—This cell, which is manufactured by Messrs. Siemens Bros. & Co., is one of the most satisfactory of those at present on the market. It is made both in the square and round forms, as shown in Fig. 130; a section of the round type is given in Fig. 131. The containing vessel Z is of zinc, and at the same time serves as the positive plate, an arrangement which is very generally

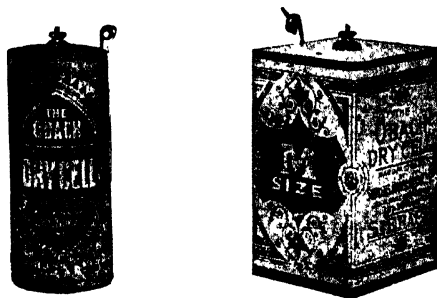


FIG. 130.—The Obach Cell.

used in dry cells. The depolariser F is made up as a stiff paste containing about 55 per cent. of manganese peroxide, 44 per cent. of plumbago, and 1 per cent. of gum tragacanth.* It is shaped into a hollow cylinder by being forced through a die, so that the round carbon rod C can be easily placed in position (original process), or the depolariser is preferably tamped in a mould around the carbon. The bottom of the zinc vessel is coated on the inside by a thin layer E of a bituminous compound on which is laid

* Ayrton, "Practical Electricity."

a disc of thick paper, thus preventing the possibility of internal short circuiting. After the carbon and the surrounding depolariser are placed centrally in position the space G is filled by pouring in a thin paste, consisting approximately of 85 per cent. of plaster-of-paris and 15 per cent. of flour, moistened with a solution of sal-ammoniac. An annulus of double canvas, I, having a large mesh, is placed above the paste, and this in turn is covered with a layer of ground

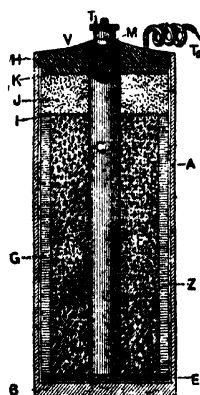


FIG. 131.—Section of Obach Cell.

- | | |
|-------------------------|-------------------------------------|
| A = Cardboard case. | H = Bituminous seal. |
| C = Carbon. | T ₁ = Positive terminal. |
| E = Insulating layer. | T ₂ = Negative terminal. |
| F = Depolarising paste. | V = Vent tube. |
| G = White paste. | Z = Zinc. |

cork, J, and a second annulus of paper, K. The zinc vessel is protected and insulated by a closely fitting cardboard case, A, having a thick base, B. This case extends higher than the zinc, which is entirely hidden by the bituminous seal H, and is therefore safe from accidental short circuit. Contact is made with the zinc by means of an insulated copper wire, T₂, soldered to it. Two small glass vent tubes, one of which is shown at V, are provided for

the escape of gases. Contact with the carbon is effected by the terminal screw T_1 which is fixed in a vertical hole drilled into the top of the carbon. This hole is enlarged at the bottom, and the screw is run in with an alloy of two parts of bismuth to one part of tin, which expands on solidifying. A nut, M, is screwed down on to the alloy, and is further held in its place by the bituminous seal. Connections are made by means of the upper terminal nut in the usual way. The square cells have the same construction, except that the zinc containing-vessel is square, as is also the depolariser which surrounds the carbon.

In Figs. 132 and 133 are reproduced some curves which were kindly furnished by Messrs. Siemens Bros. The former shows the polarisation which takes place when a cell, size B, is closed through a resistance of 5 ohms for one hour, and also the recovery of the E.M.F. during the following hour. A similar diagram was given in Fig. 38. The curves in Fig. 133 show the character of the discharge obtained from various-sized cells on a 10-ohm circuit.

The dimensions, weight, and approximate internal resistance of these cells, as given by the makers, are shown in Table I.

Table I.—*Particulars of Obach Dry Cells.*

Size.	Approximate overall dimensions. (Including terminal.)	Approximate weight of complete cell.	Internal resistance.
	Inches high.		About.
Round Cells	J $4\frac{1}{2}$ dia. $\times 9\frac{1}{2}$	9 lb. 1 oz.	0.10 ohm.
	A $3\frac{1}{4}$ dia. $\times 8$	4 lb. 0 oz.	0.15 "
	B $2\frac{1}{4}$ dia. $\times 7\frac{1}{4}$	2 lb. 6 oz.	0.20 "
	C $2\frac{1}{4}$ dia. $\times 6$	1 lb. 6 oz.	0.25 "
	D 2 dia. $\times 5$	0 lb. 14 oz.	0.30 "
Square Cells	M $4\frac{7}{8} \times 4\frac{7}{8} \times 8\frac{1}{2}$	9 lb. 10 oz.	0.15 "
	N $3\frac{1}{8} \times 3\frac{1}{8} \times 7\frac{1}{2}$	5 lb. 0 oz.	0.15 "
	O $2\frac{1}{2} \times 2\frac{1}{2} \times 6\frac{1}{2}$	3 lb. 0 oz.	0.20 "
	P $2\frac{1}{4} \times 2\frac{1}{4} \times 6\frac{1}{4}$	1 lb. 14 oz.	0.25 "
	Q $2 \times 2 \times 5\frac{1}{2}$	1 lb. 6 oz.	0.25 "
	R $1\frac{1}{2} \times 1\frac{1}{2} \times 5$	0 lb. 14 oz.	0.30 "
	S $1\frac{1}{8} \times 1\frac{1}{8} \times 4\frac{1}{2}$	0 lb. 10 oz.	0.50 "
	T $1\frac{1}{4} \times 1\frac{1}{4} \times 3\frac{1}{2}$	0 lb. 6 oz.	0.50 "

The largest of these cells is suitable for supplying a considerable current, such as that required for small glow lamps, and has been used in the well-known penny-in-the-

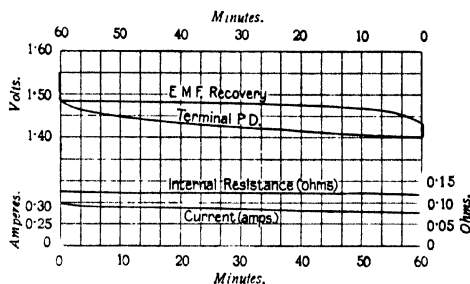


FIG. 132.—Test of an Obach Dry Cell, Size B ($2\frac{1}{8}$ in. diameter \times $7\frac{1}{8}$ in. overall, weight 2 lb. 6 oz.), closed through 5 ohms for one hour.

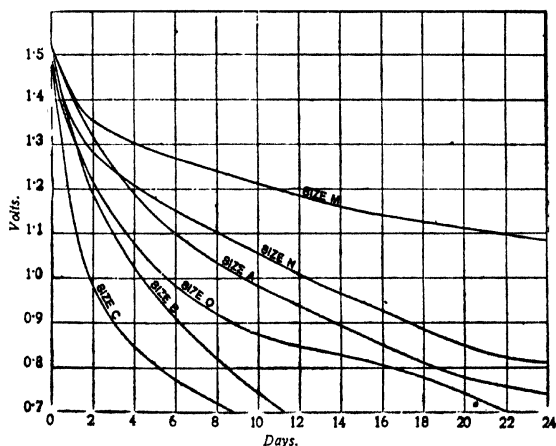


FIG. 133.—Discharge Curves of Obach Cells, closed through 10 ohms.

slot microscope machines for illuminating the photographs. Sizes B and O are usually employed on bell circuits. Smaller cells than those mentioned in the above table are

also made, and are useful for medical work and on circuits where the current required is very small.

THE HELLESEN CELL.—This cell, which is also manufactured by Messrs. Siemens Bros. & Co., was one of the first to be commercially successful. It costs somewhat less than the Obach, and size for size it has a smaller output. It is shown in section in Fig. 134. The zinc containing-

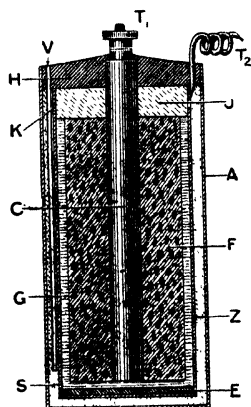


FIG. 134.—Section of Helleesen Cell.

- | | |
|-------------------------|-------------------------------------|
| A = Cardboard case. | H = Bituminous seal. |
| C = Carbon. | T ₁ = Positive terminal. |
| E = Insulating layer. | T ₂ = Negative terminal. |
| F = Depolarising paste. | V = Vent tube. |
| G = White paste. | Z = Zinc. |

vessel Z is cylindrical, and is covered at the bottom on the inside with a thin layer, E, of a bituminous insulating compound. The carbon rod C, which is round, is surrounded by the depolarising mixture F; this is held in position by canvas, forming a "sack element." The space between the depolariser and the zinc is filled in with a white paste, G. The zinc vessel is sealed with plaster-of-paris, J,

and is provided with vent holes, K. Protection is afforded to the zinc by a loosely-fitting square cardboard case, A. Since the zinc vessel is cylindrical, there is a good deal of waste space in the cardboard case, which is filled up with sawdust, S. The cell is finished off in the usual way with a bituminous seal, H, which also fills in the top of the outer case. A vent tube, V, passes through this seal into the sawdust, but there is no tube passing into the cell proper. Any gas that is formed diffuses through the plaster, passes through the holes K, and thence down through the sawdust to the vent tube. The terminal screw is fitted into the carbon in the same way as in the Obach cell.

THE E.C.C. CELL.—This cell was originally made by the Electric Construction Co., as indicated by its name, and was later supplied by the E.P.S. Co., now amalgamated with Pritchett & Gold. It is now manufactured by the Edison & Swan Co., but under a new patent, being made under H. W. Butler's patent, No. 29,065 of 1904. The patented process is briefly as follows: With the object of improving the capacity and preventing evaporation, the mass between the depolariser and the zinc is made of a starchy substance (which becomes jellified or gelatinised by the action of heat and moisture), together with a material such as cement or plaster to give the necessary consistency. For example, the mixture may be made of 20 parts of plaster-of-paris, 6 parts of ground maize and 12 parts of sal-ammoniac, with sufficient water to make it into a creamy paste. To this there may be added, say, three parts of zinc chloride. By means of a plunger this mixture is pressed into the zinc containing vessel, so as to form a lining. When it has set into a porous semi-solid mass, the plunger is withdrawn and the lining is cooked by bringing steam into contact therewith; it is then allowed to cool, the carbon is inserted and the depolariser is rammed into position.

A section of the cell is shown in Fig. 135. The carbon is flat, and is surrounded by the depolarising paste F. The special porous lining is seen at G, and is carried down as a thin layer under the depolariser, there being an insulating disc at the bottom of the cell. It will be noticed that the depolariser is kept well down below the top of the porous lining. The cell is finished off with a thick layer of sawdust, S, above which is a layer of waxed paper; the latter carries

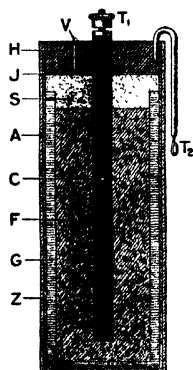


FIG. 135.—Section of E.C.C. Cell.

- | | |
|-------------------------|------------------------------------|
| A=Cardboard case. | S=Sawdust. |
| C=Carbon. | T ₁ =Positive terminal. |
| F=Depolarising paste. | T ₂ =Negative terminal. |
| G=White Paste. | V=Vent tube. |
| H=Bituminous seal. | Z=Zinc. |
| J=Layer of waxed paper. | |

the bituminous seal which makes a joint with both the zinc container and the cardboard case. A vent tube is provided.

THE G.E.C. CELL.—The construction of the G.E.C. cell, which is made by the General Electric Co. (England), is shown by Fig. 136. A zinc container, Z, is used as the electro-positive element. The carbon, C, is a flat plate, which is surrounded by a cylinder, F, of depolarising paste

of carbon and manganese peroxide, and this in turn is surrounded by the white exciting paste, G, filling up the space between the depolariser and the zinc. The exciting paste consists chiefly of plaster-of-paris and sal-ammoniac. The bottom of the zinc pot is protected from the depolariser by an insulating layer, and it will be noticed that the carbon is not carried right down. Above the paste is a layer of

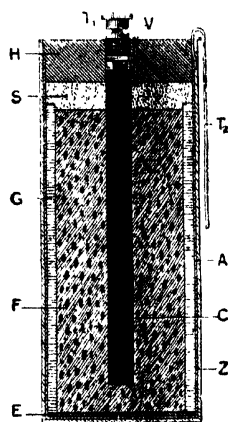


FIG. 136.—Section of G.E.C. Cell.

- | | |
|---------------------|------------------------------------|
| A=Cardboard case. | S=Sawdust. |
| C=Carbon. | T ₁ =Positive terminal. |
| E=Insulating layer. | T ₂ =Negative terminal. |
| F=Depolarising. | V=Vent tube. |
| G=White paste. | Z=Zinc. |
| H=Bituminous seal. | |

sawdust, S, and above this a bituminous seal, H, through which passes a vent tube, V. The arrangement of the terminals T₁ and T₂ is clear from the figure, the former being a common type of brass terminal and the latter an enamelled copper wire. A cardboard case, A, gives general protection.

Curves of discharge, kindly supplied to the author by the General Electric Co., are given in Fig. 137, and refer to Nos. 1 and 2 round cells.

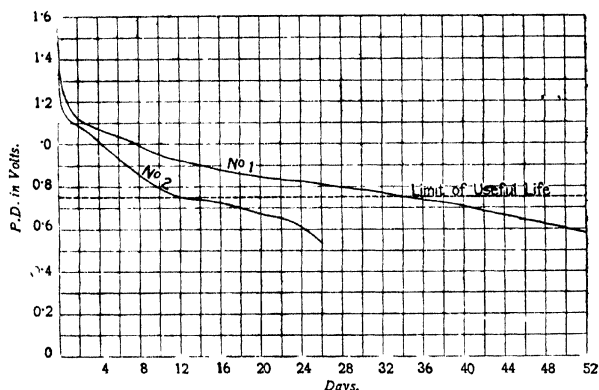


FIG. 137.—Discharge Curves of G.E.C. Dry Cells. Continuous discharge through 10 ohms external resistance.

No. 1.— $7\frac{1}{2}$ overall $\times 3\frac{1}{2}$ diam.

.. 2.— $6\frac{1}{2}$.. $\times 2\frac{1}{2}$..

Particulars of the more general sizes of G.E.C. dry cells are given in Table II.

Table II.—Particulars of G.E.C. Dry Cells.

Size.	Height over all.	Section.	Internal resistance.	Approximate capacity.
1 round	$7\frac{1}{2}$ in.	$3\frac{1}{2}$ in. diam.	0.10 ohm.	60 amp.-hrs.
2 "	$6\frac{1}{2}$ "	$2\frac{1}{2}$ "	0.15 "	25 "
3 "	$5\frac{1}{2}$ "	$2\frac{1}{4}$ "	0.20 "	12 "
00 square	$7\frac{1}{2}$ "	$4\frac{1}{2}$ in. sq.	0.10 "	120 "
1 "	$7\frac{1}{2}$ "	$3\frac{1}{2}$ "	0.10 "	70 "
2 "	$6\frac{1}{2}$ "	$2\frac{1}{2}$ "	0.15 "	34 "
3 "	$5\frac{1}{2}$ "	$2\frac{1}{4}$ "	0.20 "	15 "
4 "	$4\frac{1}{2}$ "	$1\frac{1}{2}$ "	0.30 "	5 "

THE DANIA CELL.—This cell, which is manufactured by the Atlas Carbon & Battery Co., of London, differs from

DRY CELLS.

those previously described in that the white electrolyte paste is replaced by a gelatinous electrolyte. The construction will be seen from the section in Fig. 138. Only a small layer of sawdust is used, and this is separated by impregnated paper from the electrolyte below and the seal

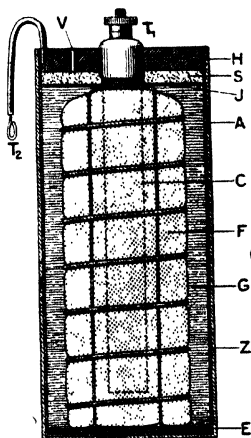


FIG. 138.—Section of Dania Cell.

- | | |
|---------------------------------|-------------------------------------|
| A = Cardboard case. | J = Paraffined paper. |
| C = Carbon | S = Sawdust. |
| E = Insulating layer. | T ₁ = Positive terminal. |
| F = Depolarising paste in sack. | T ₂ = Negative terminal. |
| G = Gelatinous electrolyte. | V = Vent tube. |
| H = Bituminous seal. | Z = Zinc. |

above. The carbon, which is round, is provided with a lead cap, and the carbon element is in the form of a sack. The cell is made in a number of sizes.

THE MANCHESTER CELL, which is supplied by Messrs. Baxendale, is similar in construction to the Dania cell.

THE E.S. CELL.—The E.S. cell is supplied by the Associated Battery Co., of London. Its main features are

shown in Fig. 139. Points of interest are that there is no insulating layer at the bottom of the zinc container; there appears to be no vent; and the seal is a double one, consisting first of sulphur and then a resinous layer.

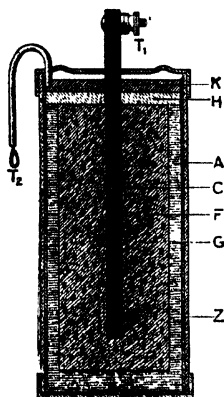


FIG. 139.—Section of E.S. Cell.

A=Cardboard case.
C=Carbon ($1\frac{1}{4}$ in. \times $\frac{3}{8}$ in.)
F=Depolarising paste.
G=White paste.
H=Layer of sulphur.

K=Resinous seal.
T₁=Positive terminal.
T₂=Negative terminal.
Z=Zinc.

THE LESSING CELL.—The cell devised by Lessing differs from those hitherto described in that the containing vessel is not the zinc plate of the cell, but is an opal glass jar. This has the disadvantage that the cell is more liable to be injured, but the zinc is made more simply, being in the form of a cylindrical sheet, part of which extends beyond the seal so as to carry the negative binding screw T₂ (see Fig. 140). The zinc is coated on the outside with black insulating varnish. The carbon plate C, which is shown edgewise in the Figure, is made unusually wide, so that the depolarising mixture, F, practically forms a

semi-cylinder on each side of it, leaving the edges exposed. This mixture is kept in place by being wound round with canvas. A white paste, G, fills up the space between the depolarising paste and the zinc, and also any space between the zinc and the containing jar. The paste is covered with a thick layer of sawdust, S, above which is a protecting

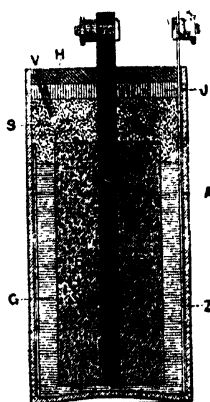


FIG. 140.—Section of Lessing Cell.

A = Glass Containing Vessel. T₁ = Positive terminal.
 C = Carbon. T₂ = Negative terminal.
 F = Depolarising Paste. V = Vent Tube.
 G = White Paste. Z = Zinc.
 H = Bituminous Seal.

layer of a white porous material, J, and finally the ordinary bituminous seal, through which there passes a metallic vent tube, V. Both terminals are of the screw type, held in position by a nut.*

* The description of this cell remains as it was in the last edition of this work owing to the impossibility (due to the European war) of obtaining further information at the time of revision.

THE LE CARBONE (HUDSON) CELL.—There are some noticeable differences between the cell made by Le Carbone and those previously described. Thus, a black glass jar is used as the containing vessel, the zinc being merely a sheet bent into cylindrical form, on the lines of the Lessing cell. The zinc is kept spaced away from the sack element by means of vertical pieces of cord tied on the latter. Instead of a white paste, a gelatinous electrolyte is used,

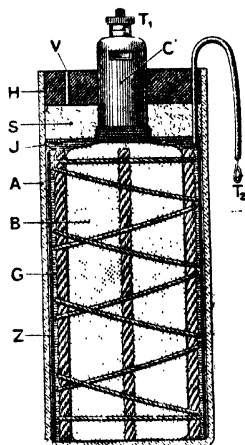


FIG. 141.—Section of Le Carbone (Hudson) Cell.

- | | |
|-----------------------------|-------------------------------------|
| A = Glass jar. | S = Sawdust. |
| B = Sack element. | T ₁ = Positive terminal. |
| C = Carbon. | T ₂ = Negative terminal. |
| G = Gelatinous electrolyte. | V = Vent tube. |
| H = Bituminous seal. | Z = Zinc. |
| J = Layer of wax. | |

and fills up the intervening space between the sack and the containing jar. There is a tin layer of wax between the gelatinous electrolyte and the sawdust, but the bituminous seal appears to be poured directly upon the sawdust. Details of this cell are shown in Fig. 141.

THE R. & R. CELL.—This cell, which is made by Messrs. Rylander and Rudolphs, of Henriksdal, Sweden, is interesting in that it depends to some extent on atmospheric oxygen for its depolarising qualities. From Fig. 142 it will be seen that a hollow carbon is used for this purpose. The cell is square, and the carbon element is made up in sack form of square section, the top and bottom being strengthened by cardboard. Round the carbon element is a gelatinous electrolyte. The zinc containing-vessel acts as one

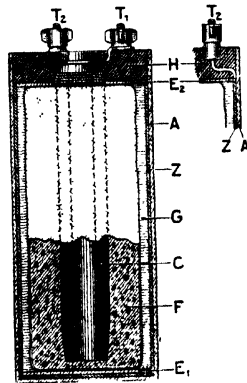


FIG. 142.—Section of R. & R. Cell, showing the sack element partly in section.

- | | |
|---|------------------------------------|
| A=Cardboard case. | H=Bituminous seat. |
| C=Carbon. | T ₁ =Positive terminal. |
| E ₁ , E ₂ =Layers of cardboard. | T ₂ =Negative terminal. |
| F=Depolariser in sack. | Z=Zinc. |
| G=Gelatinous electrolyte. | |

electrode, and is protected externally by a cardboard case. It is noticeable that the zinc container only extends up to the under side of the seal. The latter makes a joint with the cardboard case above the zinc container. There is no vent. The terminal T₂ is fixed away from the container; it is connected thereto by a strip of zinc, and is embedded in the seal, as shown by the detail to the right of Fig. 142. The

other terminal is carried by a ring of sheet brass which is forced on to the conical end of the carbon. The cell is stocked with the carbon well corked.

The possibility of atmospheric oxygen playing a part in supplementing the available oxygen in the manganese peroxide in the Leclanché type of cell seems to have been pointed out by Holst; but Rudolphs appears to have been the first to devise a dry cell in which this idea is put seriously into practice. In Fig. 143 are reproduced two curves published by the makers of the R.R. cell, showing the gain that is found when the carbon is left open. The curve A refers

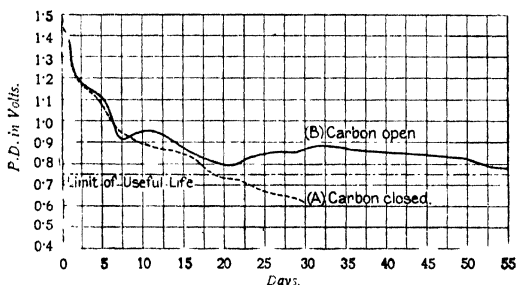


FIG. 143.—Discharge Curves of R. & R. Cell, showing the effect of atmospheric absorption.

Continuous discharge through 10 ohms external resistance.

to the case when the carbon is left corked. Under these conditions the P.D. fell to 0.75 volt in 18 days. On the other hand, when the top of the carbon was left open, this limit had not been reached after 55 days. It is therefore concluded that atmospheric oxygen plays an important part. The effect becomes increasingly important as the manganese peroxide is reduced by the action of the cell. Without, however, knowing precisely how the maker's experiments were carried out it is only possible to discuss the point briefly.

THE BLUE BELL CELL.—Passing now to American cells, we find that a cheaper form of construction is generally adopted in the United States. Thus, a sack element is no longer used and an electrolyte paste is omitted, its place being taken simply by a layer or two of absorbent paper, as mentioned earlier in this chapter.

In the Blue Bell cell, which is used exclusively by the Western Electric Co. for their telephone work, these features

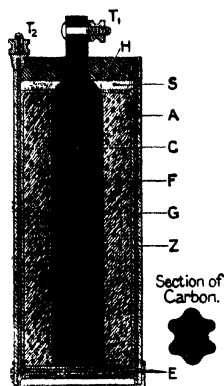


FIG. 144.—Section of Blue Bell Cell.

- | | |
|------------------------------|------------------------------------|
| A=Cardboard case. | H=Bituminous seal. |
| C=Carbon. | S=Layer of sand. |
| E=Three layers of pulpboard. | T ₁ =Positive terminal. |
| F=Depolarising paste. | T ₂ =Negative terminal. |
| G=Absorbent paper. | Z=Zinc. |

are evident, as seen by the section in Fig. 144. The carbon is of the unusual form shown in the small section on the right-hand side of this figure, the idea being, presumably, that better contact is thus obtained with the depolarising paste. The zinc case is provided with a small acorn-head post with screw terminal instead of a wire. The absorbent paper which lines the zinc is folded down over the top of the

depolariser paste; and this is covered with a layer of fine sand, over which the bituminous seal is poured. No vent appears to be provided in this cell.

Test curves of the Blue Bell cell, as obtained by the National Physical Laboratory, are reproduced in Fig. 145,

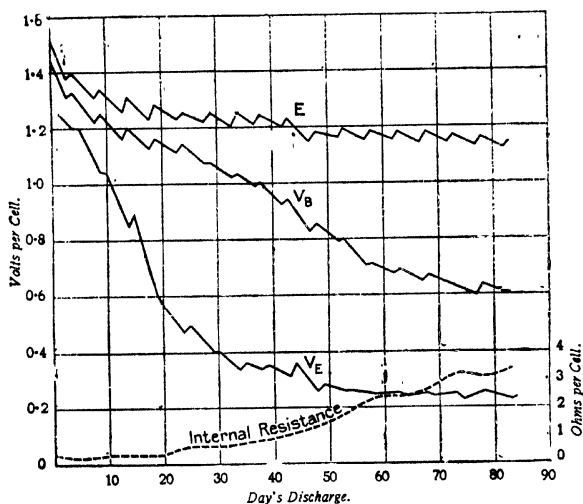


FIG. 145.—Discharge Curves of Blue Bell Cell. (Natural Physical Laboratory—6 cells.)

Intermittent test on 5 ohms for 6 hours per day; resting the other 18 hours and also resting on Saturdays and Sundays.

Size of Cell:—

E = E.M.F. before beginning of Daily Discharge.

V_b = P.D. at beginning of Daily Discharge.

V_e = P.D. at end of Daily Discharge.

and are of interest as showing the capabilities of a cell of this kind on a test designed for telephonic purposes.

THE COLUMBIA CELL.—This cell is one of the best known American dry cells, and is made by the National Carbon Co., of Cleveland, Ohio. From the section shown

in Fig. 146 it is seen that the zinc container is lined with absorbent pulpboard, and this is made to surround the depolarising paste entirely. The cell is finished off, first, with a layer of sawdust, over which is an air space, then a layer of sand, and finally a bituminous seal. The air space is maintained by a collar punched out of corrugated paper, and serves as a reservoir into which surplus electrolyte can

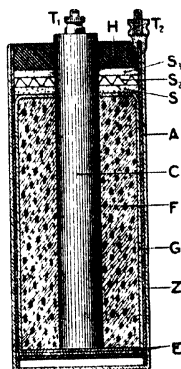


FIG. 146.—Section of Columbia Cell.

- | | |
|------------------------|---|
| A=Cardboard case. | S ₁ =Layer of sawdust. |
| C=Carbon. | S ₂ =Corrugated cardboard collar |
| E=Layers of pulpboard. | S ₃ =Layer of sand. |
| F=Depolarising paste. | T ₁ =Positive terminal. |
| G=Absorbent pulpboard. | T ₂ =Negative terminal. |
| H=Bituminous seal. | Z=Zinc. |

be forced when heavy currents are taken. When the discharge stops, the electrolyte runs back. The air space takes the place of a vent.

THE JOVE CELL.—This cell, again, is of American manufacture, being supplied by Messrs. J. H. Bunnell & Co., of New York. The main features are shown in Fig. 147. It is noticeable that the absorbent paper lining to the zinc case is not folded down over the top of the depolarising paste.

A little sawdust is sprinkled over the top of the latter, and then the bituminous seal is run in without protection. There appears to be no vent. The round carbon terminates in a brass cap which carries the terminal.

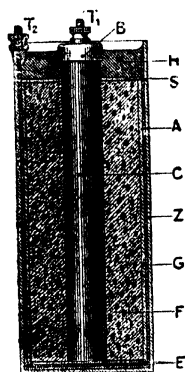


FIG. 147.—Section of Jove Cell.

A=Cardboard case.
B=Brass terminal cap, round.
C=Carbon.
E=Layers of cardboard.
F=Depolarising paste.
G=Absorbent paper.

H=Bituminous seal.
S=Sprinkling of sawdust.
T₁=Positive terminal.
T₂=Negative terminal.
Z=Zinc.

THE MASCOT CELL is another American dry cell supplied by the same makers, Messrs. J. H. Bunnell & Co.

DESICCATED CELLS.

It is well recognised that dry cells deteriorate if they are in a hot place considerably more quickly than if kept in a place that is cool. It is not surprising, therefore, that such cells are found less satisfactory in tropical than in temperate climates. For this reason cells have been devised which are not only dry by name but dry in actuality, and may thus be called desiccated cells. Substantially, these cells are dry cells in which powders are used instead of pastes. Con-

sequently, they can be kept indefinitely without deterioration, and when they are required for use the necessary water can be added. This is a very great advantage ; but, on the other hand, such cells do not in all cases have as long a life as the corresponding dry cells.

THE "EXTRA SEC" CELL.—This cell, which is made by the General Electric Co., may be described as a G.E.C. dry cell modified to take advantage of the above principles.

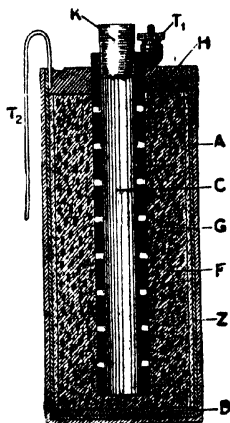


FIG. 148.—Section of the "Extra Sec" Cell.

- | | |
|-----------------------------|------------------------------------|
| A=Cardboard case. | H=Bituminous seal. |
| B=Insulating layer. | K=Rubber cork. |
| C=Carbon tube. | T ₁ =Positive terminal. |
| F=Depolarising paste | T ₂ =Negative terminal. |
| G=Layer of absorbent paper. | Z=Zinc. |

A section of the cell is shown in Fig. 148. A tendency towards American practice is seen in that a thick layer of absorbent paper is used for lining the zinc container. The space between the paper and the carbon is filled with the depolarising mixture. The carbon is in the form of a perforated carbon tube, so that when water is poured into this tube it percolates through the perforations and saturates the depolarising mixture ; the latter is made up with exciting

salts, so that the necessary electrolyte is produced when the water is added.

According to data published by the Company, the life of this cell is not so high as that of the corresponding dry cell. As to what is the explanation of this shorter life it is difficult to say with certainty. Possibly it may be due to the fact that the lower oxide produced by the reduction of the manganese peroxide is more bulky. Since the paper is much less yielding than the white paste or gelatinous electrolyte used in dry cells, the resulting pressure may be high enough to force the moisture out of the paper and to form the impurities from the zinc into a layer of somewhat high resistance, thus shortening the life.

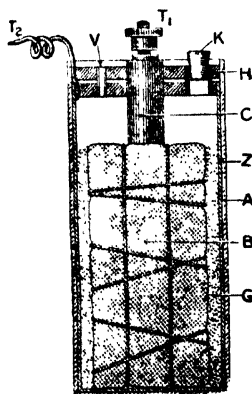


FIG. 149.—Section of the Dura Cell.

- | | |
|--------------------|------------------------------------|
| A=Cardboard case. | K=Cork stopper. |
| B=Sack element. | T ₁ =Positive terminal. |
| C=Carbon. | T ₂ =Negative terminal. |
| G=Excitant powder. | V=Vent tube. |
| H=Cork seal. | Z=Zinc. |

THE DURA CELL.—The Dura cell, which is made under a patent by Messrs. Siemens Brothers & Co., is more of the wet-cell type. As will be seen from Fig. 149, a sack form

or carbon element is used, and the space between this and the zinc container is filled with a powder consisting of ammonium chloride and a gelatinous substance which forms a paste when moistened. There is a considerable space between the top of the sack and the seal. The latter consists of two layers of cork, the lower one of which closes the zinc vessel and the upper one the outer case, the space between these two layers being filled with a resinous material. A vent tube is provided, and also a corked tube, through which water is added. The cell is charged by pouring in water until the cell is full. It is then allowed to stand for a few hours, when any water that has not been absorbed is shaken out and the tube is re-corked.

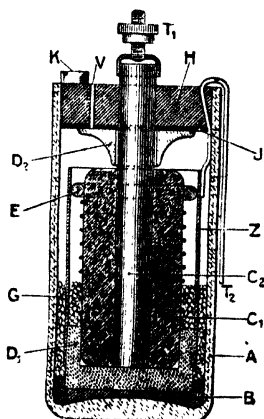


FIG. 150.—Section of H.2O Cell.

- | | | |
|----------------------------------|----------------------------------|-------------------------------------|
| A = Glass jar. | D ₂ = Porcelain ring. | K = Cork. |
| B = Layer of compound. | E = Rubber ring. | T ₁ = Positive terminal. |
| C ₁ = Sack element. | G = Excitant crystals. | T ₂ = Negative terminal. |
| C ₂ = Carbon. | H = Bituminous seal. | V = Vent tube. |
| D ₁ = Porcelain base. | J = Waxed cardboard washer. | Z = Zinc. |

THE H.2O CELL.—This cell, which is rather more complicated in its construction than the other examples here described, is made by the Ediswan Co. As shown by Fig. 150,

a glass jar is used as a container. Into the bottom of the jar is run a little bituminous compound, which serves to fix a porcelain cup. The latter acts as a support for the sack element. The cylindrical zinc is separated from the sack at the bottom by the porcelain cup, and at the top by a rubber ring. Above the sack is a porcelain ring, which carries a waxed cardboard washer for supporting the bituminous seal. A vent tube is provided in the seal. An unusual feature is the strip terminal connection to the zinc, which is of lead; the other terminal is fixed by means of a brass cap. The cell contains a certain quantity of crystals and only requires the addition of water.

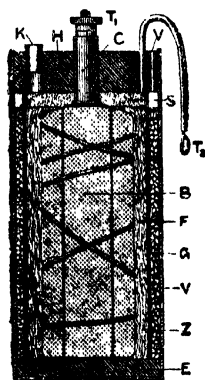


FIG. 151.—Section of the Reliable Cell.

- | | |
|------------------------|-------------------------------------|
| B = Sack element. | S = Sawdust. |
| C = Carbon. | T ₁ = Positive terminal. |
| F = Insulating layer. | T ₂ = Negative terminal. |
| G = Turkish towelling. | V = Vent tube. |
| H = Bituminous seal. | Y = Galvanised-iron container. |
| K = Corkstopper. | Z = Zinc. |

THE RELIABLE CELL.—This cell is made by the Associated Battery Co., and has some unusual features. The container is of galvanised iron instead of zinc, and is

covered on the outside with a paper wrapper. It is protected internally at the bottom by a thick bituminous layer, and the walls are also protected by a bituminous coating. This container is rectangular in section. The carbon element is in the form of a sack, and surrounding this is a cylindrical sheet of zinc. Between the sack and the zinc is a layer of Turkish towelling, and the space between the zinc and the container is packed with excitant crystals. The cell is finished off with a layer of sawdust, then some thin canvas and finally a bituminous seal, through which there is a corked aperture on the one side and a vent on the other, as seen in Fig. 151.

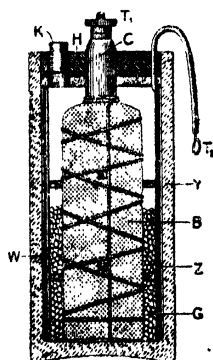


FIG. 152.—Section of the W.O. Cell.

- | | |
|------------------------|-------------------------------------|
| B = Sack element. | T ₁ = Positive terminal. |
| C = Carbon. | T ₂ = Negative terminal. |
| G = Excitant crystals. | W = Sheet of paper. |
| H = Bituminous seal. | Y = Earthenware jar. |
| K = Cork stopper. | Z = Zinc. |

THE W.O. CELL.—The W.O. cell, which is made by the Atlas Carbon & Battery Co., differs from the cell last described in that an earthenware jar is used as the container. The sack element is surrounded by a cylindrical sheet of zinc, and between the two is a sheet of paper. This space

also contains exciting salts. The cell is finished off with a layer of sawdust and a bituminous seal, there being a layer of cardboard both above and below the sawdust. No vent is provided. A section of the cell is given in Fig. 152.

THE BURN-BOSTON CELL.—This cell is an American example of the dessicated type, being made by the Burn-

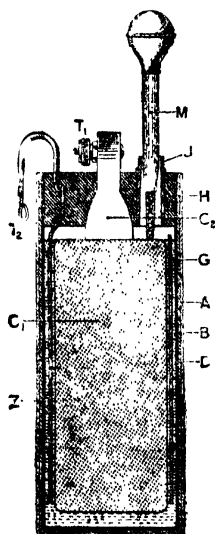


FIG. 153.—Section of Burn-Boston Cell.

- | | |
|-------------------------------|------------------------------------|
| A=Paper case. | H=Seal. |
| B=Zinc container. | J=Filling tube. |
| C ₁ =Sack element. | M=Medicine dropper. |
| C ₂ =Carbon. | T ₁ =Positive terminal. |
| D=Insulating layer. | T ₂ =Negative terminal. |
| G=Electrolyte. | Z=Zinc element. |

Boston Battery & Mfg. Works, of Boston. The construction is shown in Fig. 153. The zinc containing-vessel, which is of the square form, is protected externally by a waterproof paper cover and is coated internally with an

insulating compound, so that it takes no part in the voltaic action, and consequently is not subject to corrosion. A separate zinc plate is provided. The carbon element is of the sack form, and the cell is completed by a bituminous seal which carries a tube. This is closed by a cap having a pinhole vent at the top. The cell is sent out containing the necessary exciting salts, and is filled with water by means

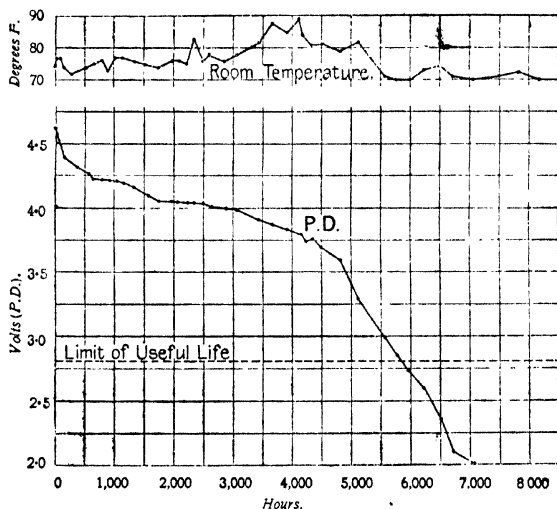


FIG. 154.—Discharge Curve of Burn-Boston Cell on Standard Telephone Test of the American Electrochemical Society. (Electrical Testing Laboratories.)

of a medicine dropper, as shown. There should be an air space above the carbon element. The simplest way of filling is, therefore, to run in a little too much water and then remove as much as possible by the medicine dropper.

The cell can be recharged by running out the solution and filling with electrolyte, as distinct from water. Cells are

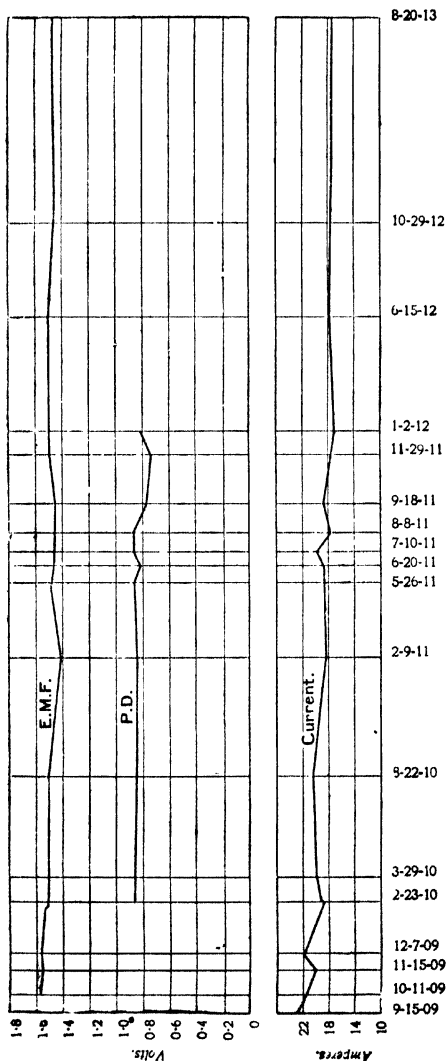
also being made in which the zinc and carbon can be renewed. For this purpose, a cork cover is used in place of the seal, and makes a tight joint with the carbon and container.

A test of Burn-Boston cells by the Electrical Testing Laboratories of New York, according to the standard telephone test of the American Electrochemical Society, is given in Fig. 154.

An unusually long deterioration test (four years) of these cells has been made by the Bay State Street Railway Co. (U.S.A.) and is reproduced as a diagram in Fig. 155. From this it will be seen that the deterioration is very slight. These tests refer to a cell which was filled at the beginning of the period and left untouched thereafter.

In this connection it should be noted that some desiccated cells, when filled with water, become equivalent to dry cells, whereas others are more truly described as wet cells, and the characteristics will, therefore, vary accordingly. The Burn-Boston cell tends to the wet type, and consequently the deterioration with age should be very small (as it is), provided, of course, that evaporation of the electrolyte can be avoided, or that this liquid is of such a nature that it maintains its strength constant by the inclusion of suitable deliquescent materials.

COMPARISON OF WET AND DRY CELLS.—A comparison of the performances of wet and dry Leclanché cells reveals the fact that dry cells are superior from the point of view of capacity for a given weight. In order to obtain such a comparison it is, perhaps, best to rely upon the data given in any one maker's list (rather than on a variety of tests) so as to compare cells which are presumably of the same standard of manufacture for all types and are, therefore, fairly comparable. The following table has been prepared on this basis, cells of the General Electric Co. being selected



• Fig. 155.—Deterioration Tests of Burn-Boston Cell over a Period of Four Years.

The cell was subjected to test on certain dates, most of which are indicated. On these dates the cell was short-circuited through a resistance of approximately 0.01 ohm for 10 seconds, and the maximum currents observed on each occasion are shown by the lowest curve. The top curve shows the E.M.F. and the middle curve shows the potential difference at the end of a 10-second period, when the cell was discharged through a resistance of $\frac{1}{4}$ ohm.

for the purpose. The weight of wet cells can only be stated very approximately, as this varies with the amount of, and strength of, the electrolyte. By "useful life" is meant the number of days taken for the voltage of the cell to fall to 0.75 volt when run continuously on a 10-ohm circuit. The last column gives the figure obtained by dividing the useful life by the weight of the cell, or, in other words, the life per pound.

Table III.—Comparison of Wet and Dry Cells.

Type of Cell.	Weight. (Approx.)	Size. (Overall.)	Useful life in days.	Useful life ÷ weight.
<i>Wet Cells.</i>				
Porous Pot Leclanché (pint)...	2½ lb.	3½" × 3½" × 6½"	3½	1.3
Carporous (pint)	4½ lb.	4" × 4" × 7½"	4	0.95
Carsak (pint)	4½ lb.	4" × 4" × 7½"	15	3.5
Porous Pot Leclanché (quart) ..	4½ lb.	3½" × 3½" × 7½"	7½	1.6
Agglomerate Block (quart) ...	4 lb.	3½" × 3½" × 7½"	4½	1.1
Carporous (quart)	6 lb.	4½" × 4½" × 8½"	11	1.8
Carsak (quart)	6½ lb.	4½" × 4½" × 7½"	39	6.2
Porous Pot Leclanché (3-pint)...	7 lb.	4½" × 4½" × 8½"	17½	2.5
Agglomerate Block (3-pint)...	6½ lb.	4½" × 4½" × 8½"	10½	1.7
6-Block Agglomerate (3-pint)...	11½ lb.	6" diam. × 9½"	17½	1.6
Carporous (3-pint).....	8 lb.	4½" × 4½" × 9½"	16	2.0
Carsak (3-pint)	8½ lb.	4½" × 4½" × 8½"	81	9.3
<i>Dry Cells.</i>				
No. 3 G.E.C. square	1lb. 11oz.	2½"sq. × 5½"high	7½	4.4
No. 2 G.E.C. square	2lb. 12oz.	2½"sq. × 6½"high	15½	5.6
No. 1 G.E.C. square	5 lb.	3½"sq. × 7½"high	32	6.4

From these figures can be seen the great advantage of the sack form of cell over the other types of wet cell. Agglomerate cells do not show up so well as the ordinary porous pot cells on this basis. It is noticeable that the dry cells are much superior to the wet cells, and that this superiority is obtained with a smaller weight. Thus, the No. 1 dry cell weighs only 5 lb., whereas the average 3-pint wet cell weighs 8 lb. and gives a considerably less efficient result. The No. 1 dry cell has about the same weight as the average quart-size wet cell. It is seen that the efficiency in all types generally increases with the size of cell.

In the matter of first cost, wet cells generally have an advantage. For example, the list price of a No. 1 G.E.C. cell is 3s., whereas the prices of the 3-pint wet cells are 1s. 10½d., 2s. 3d. and 3s. 9d. for a porous pot cell, an agglomerate block, and a carporous respectively. The price of a 6-block agglomerate is 5s. 6d., but that of a 3-pint Carsak cell is only 3s.

A dry cell has the disadvantage that when it is exhausted it is of no further use and must be thrown away, unless the manufacturing company makes an allowance for old cells, which is sometimes the case. Wet cells can, of course, be re-charged when exhausted. But, as shown in Chapter VIII., the mere addition of fresh electrolyte does very little to put new life into an exhausted cell. It is necessary to renew the depolarising material as well, and not infrequently the zinc also. Consequently the supposed advantage of being able to re-charge a cell is not a very great one, and, on the other hand, the dry cell is greatly superior in that it is always ready for use and is exceedingly easy to handle.

TESTING DRY CELLS.

The testing of dry cells has assumed some importance as a distinct branch of cell testing owing to the fact that these cells are used in enormous quantities and for very different classes of service. For this reason a good deal of attention has been given to the subject.

The object of tests is generally to obtain *comparative* results, so that one kind of cell may be compared with another, or so that different batches of the same kind of cell may be compared so as to ensure a certain standard of manufacture. Unfortunately, different kinds of tests do not always lead to the same comparative results, and therefore a test should be selected having some relation to the character of the work for which the cell is required. Thus

for some purposes an intermittent test may be preferable to a continuous test. It need scarcely be remarked that the precise service conditions under which a cell is to be used can rarely if ever be reproduced as test conditions, and even if they could the test would be too prolonged to be useful. But it is desirable to be able to deduce the life in service from the life on test with some show of probability.

Apart from comparative life tests, other tests are used to determine whether a cell is in good condition and whether it deteriorates on open circuit.

TESTS TO DETERMINE THE CONDITION OF A CELL BEFORE USE.—These tests include the measurement of E.M.F. (which should be not less than 1.5 to 1.6 volts) and internal resistance. Such information is not of any great value, and sufficient has been said on these measurements in a previous chapter to afford a guide in the present tests.

A third test is what is known as the **Short Circuit Test**. It is in common use in the United States, but it has been subjected to a great deal of criticism on the ground that it may be harmful to the cell and gives information of only doubtful value. Taking the average American cell, which is 6 in. high by $2\frac{1}{2}$ in. diameter, it is found that the current on short-circuit, when the cell is new and good, varies from 18 to 25 amperes. Inferior cells give currents as low as 10 amperes. This remark, however, does not apply to English cells. American practice and English practice differ so much that the product of these countries cannot well be compared. In the former everything seems to be sacrificed to high initial current, whereas in this country the best qualities and preparations of materials are selected with a view to producing a cell with the longest useful life. ● A current ranging from 5 amperes in the middle sizes to 12 amperes in the large sizes is undoubtedly sufficiently high for ordinary requirements, and dry cells can be made which

give such currents on the short-circuit test, and will give also a maximum output and possess the useful characteristic of maintaining their condition when kept in store for a very long time.

This test gives an easy means of determining if a cell is in good condition, provided the behaviour of the particular brand of cell is known. It also forms the basis of what is called the **Shelf Test**. The longer a cell is kept in stock the smaller is the short-circuit current. In the United States it is considered that the short-circuit current

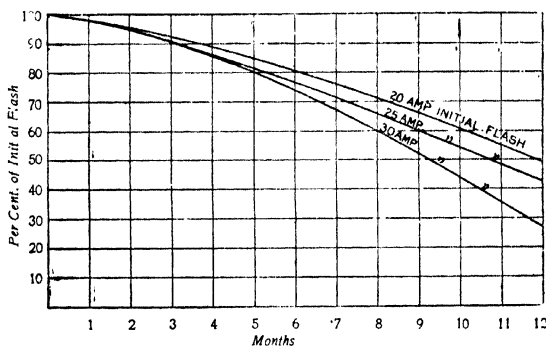


FIG. 156.—Variation of Short-Circuit Current with Age of Cell.
(Hambuechen.)

should not fall below 10 amperes after storing ("on the shelf") for about 12 months. The curves in Fig. 156 are given by C. Hambuechen* as showing the variation of the short-circuit current as a cell is stored.

For the short-circuit test to have any true meaning it is necessary that the ammeter should have a definite resistance; otherwise the results might vary with the ammeter selected. A committee of the American Electrochemical

* *Transactions, American Electrochemical Society*, Vol. XXI, p. 297.

Society have recommended that the resistance, including the leads, should be 0.01 ohm, correct to within 0.002 ohm. Connection must be made by the cell terminals, and it is suggested that the maximum swing of the needle should be taken as the short-circuit current. This direction should scarcely be necessary, as a very dead beat instrument should be used and the circuit should be closed only just long enough to secure a reading. It is stated to be an advantage if the leads terminate in a strip of lead, as this improves the contact with the terminals.

The value of the short-circuit current depends appreciably upon the temperature. It is found that the current rises (for the size of cell above mentioned) by about 1 ampere for each 10°C. rise in temperature between 10°C. and 80°C. Cells are particularly sensitive in this way at low temperatures.

Shelf life is affected considerably by temperature. This fact is illustrated by the figures in Table IV., which are given by D. L. Ordway.* They refer to cells tested after keeping for five months at the temperatures indicated.

Table IV.—*Effect of Temperature on Shelf Life of Cells (6 in. \times 2½ in. diameter).*

Temperature at which cells were stored.		Short-circuit current at 25°C. after 5 months.
0°	18.1
25°	17.4
50°	0.5
75°	0.4

There is, therefore, good reason for storing cells in a cool place.

The short-circuit test, although it gives an indication of age or defective condition, gives no measure of the service capacity. The figures in Table V., due to D. L. Ordway,†

* *Transactions, American Electrochemical Society*, Vol. XVII, p. 341.

† *Loc. cit.*

illustrate this point. Here the "old" cells were nine months old, and the capacity was found by discharging continuously on a 2-ohm circuit down to 0.25 volt.

Table V.—*Short-circuit Current and Service Capacity of New and Old Cells.*

	New Cells.		Old Cells.	
Short-circuit current ...	22.4 amperes	...	3.6 amperes.	
* Service capacity	24.9 ampere-hours...		20.2 ampere-hrs.	

On the other hand, the short-circuit current obviously gives an indication of the internal resistance, and for this reason some conclusions may be drawn as to the ingredients in the case of a new cell. For example, if the current is unduly high we may conclude that an excessive amount of low resistance carbon or graphite has been included, thus reducing the manganese peroxide below the proportion which is desirable for good depolarisation. But if the current is unduly low it is probable that cheap materials have been used.

The short-circuit test, although commonly used in the United States, has not found much favour among English manufacturers or users. Dry cells are not intended to give large currents, and it is felt that indiscriminate testing by short-circuits can do no good to a cell and may do harm. Moreover, such a test is not a measure of the life obtainable; in fact, if the current is above a certain figure the output in service will probably be low.

LIFE TESTS.—There is much to be said for simplicity in tests, and for this reason a continuous test, by running on, say, 10 ohms, has been popular. Results are sometimes stated in ampere-hours or in watt-hours, but generally the user is more concerned simply with time. In other words, cells are generally used on constant resistance circuits, and so long as the current is maintained above a certain value the result is satisfactory; but current above this value, and

the voltage necessary for this excess, are merely so much waste from the user's point of view. Hence time, rather than ampere-hours or watt-hours, is important.

For some purposes, such as ignition, cells may be tested in series, but generally speaking it is preferable to test cells singly, rather than in series, because the average obtained by the series arrangement is not necessarily the same as the average obtained by testing the cells separately and averaging the results.

Reliance should not be placed on a small number of tests. If the comparison is important it is better to run a series of tests over six months or a year. The following results (due to W. B. Pritz) of 10 monthly tests on two brands of cell illustrate this point * :—

No. of Test	1	2	3	4	5	6	7	8	9	10	Average
Brand A	42	35	38	33	60	45	48	35	66	48	45.0
Brand B	30	37	24	25	27	40	48	42	40	40	35.3

On a continuous test the character of the curve depends upon the value of the resistance that is used for the circuit. If the resistance is low, say, 2 ohms for an ordinary size cell, the voltage falls rapidly because the depolarisation is insufficient to meet the needs of the case. With a high resistance the fall is much less rapid. A low resistance test would not be used for testing a cell intended to be used for only small currents.

The effect of an intermittent test is to give a cell time to recover and consequently the result obtained is materially different from that obtained by a continuous test. This is emphasised by the curves in Fig. 157, which are due to D. L. Ordway.† These tests refer to a circuit of 10 ohms, the results being obtained with three cells in series on each

* Report of Committee of American Electrochemical Society. Also W. B. Pritz. *Transactions, American Electrochemical Society*, Vol. XIX., p. 31, 1911.

† *Loc. cit.*

test. Curve A shows a continuous test, whereas curve B refers to a test in which the cells were on circuit for five minutes in each hour. Only the times the cells were on circuit are taken into account in plotting the results, and consequently the hours shown are not unduly long. In the case of curve C the conditions are the same as for curve B except that the test was only run for eight hours per day and for six (or even fewer) days per week, or in other words the time for recuperation was increased and the total time for the test (including the intervals of rest) was longer. It is noticeable that cells on intermittent service are able to

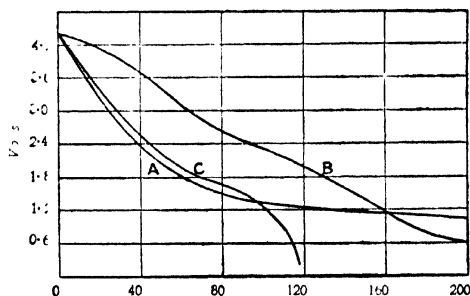


FIG. 157.—Comparison of Intermittent and Continuous Tests, Three Cells, through 5 ohms External Resistance. (Ordway.)

Curve A. Continuous Discharge.

" B Discharge of 5 minutes in each hour.

" C Do. but for only 8 hours per day and six (sometimes five) days per week. The time taken is that actually on circuit.

stand up better than on continuous use for a considerable time, but eventually the position of affairs is reversed. Curiously enough, when the intervals are increased, as in curve C, the result is not so good. This is apparently due to the fact that the time of the test is then so far extended that deterioration of the cell sets in through ageing, and this view is supported by the fact that both curves B and C fall more quickly below curve A as the resistance of the circuit

is increased (*e.g.*, if a circuit of 20 ohms is used instead of 10 ohms), the duration of the test being thereby extended. It must be borne in mind that water is formed in the action of a cell and thus a discharge up to a certain value may be beneficial in keeping a cell in condition. Whereas if only small discharges are taken at long intervals a cell tends to suffer from ageing to a greater extent.

Similarly, it will be understood that the service capacity of a cell depends upon the temperature at which it is used. The life is increased by raising the temperature if the service is heavy. But if the service is light a low temperature is preferable so as to reduce the effect of ageing. This is shown by the results in Table VI., due to D. L. Ordway.* In these tests the cells were discharged down to 0.5 volt, and it will be noticed that the temperature at which the maximum life is obtained varies with the current taken from the cell.

Table VI.—*Effect of Temperature on Life of Cells (6 in. \times 2½ in. diam.)*

Temperature at which cells were tested.		Life on 2 ohm circuit.		Life on 32 ohm circuit.
0°C.	40 hours	1,800 hours.
25°C.	60 "	1,550 "
50°C.	70 "	1,250 "
75°C.	65 "	1,390 "

That the comparative results may vary considerably according to the test adopted is shown by the results in Table VII. These were obtained by S. W. Melsom† at the National Physical Laboratory. Four types of cell were selected, the size being 7 in. by 2½ in. by 2½ in. Four cells of each make were submitted to each test. In the Table, the type A is regarded as giving 100 per cent. value and the other types are expressed in terms of this. It will be noticed that generally, though not always, the order of merit is the

* *Loc. cit.*

† *Transactions, Faraday Society, Vol. VIII, p 1, 1912.*

Table VII.—*Relative Capacity of Cells at Various Rates of Discharge* (S.W. Melsom). (The values are in watt-hours, except where otherwise stated. V.B. means P.D. at beginning of daily discharge, and V.E. means P.D. at end of daily discharge.)

Test No.		Cells.			
		A.	B.	C.	D.
1	5 mins. per hour on 50 ohms to 0.9 volt	100	93	83	28
2	5 mins. per hour on 1 ohm. Cells new.	100	59	43	7
	Ditto after 6 months' storage	100	58	50	...
	Ditto after 12 months' storage	100	53	42	...
	Six hours per day on 5 ohms—				
3	By V.E.	100	71	68	47
	By mean of V.B. and V.E. curves ...	100	50	50	35
	Continuous at 20 milliamperes—				
4	By ampere-hours. Cells new	100	43	36	30
	By watt-hours. Cells new	100	45	40	29
	By watt-hours after 8 months' storage	100	50	45	5
	Continuous on 10 ohms—				
5	To 0.7 volt	100	75	53	60
	To 0.5 volt	100	71	55	60
	To 0.7 volt after 6 months' storage...	100	59	44	28
	To 0.7 volt after 12 months' storage	100	67	50	2
6	Continuous on 100 ohms to 0.9 volt...	100	68	51	35
7	Continuous on 500 ohms to 1.3 volts	100	102	87	10

same in all the tests, but the extent to which one type is better or worse than another varies a great deal. For example, type D was consistently low except in test 5. It is evident that some cells show up better on a continuous than on an intermittent test, and *vice versa*. This point is emphasised by Table VIII., in which the watt-hours are given for the different types. It should be noted that the voltage limits are not the same for all the tests, and this in itself will cause some differences, but the variations are in many cases much greater than can be accounted for in this way. Cells A, C and D all give the maximum output on the intermittent test of six hours per day, but cell B gives its maximum on a continuous test on 100 ohms.

As to what test should be employed depends on the nature of the work for which the cell is required. A Committee of

Table VIII.—*Showing the Effect of the Different Tests given in Table VII. on the Capacity Expressed in watt-hours.*

Test No.	Cells.			
	A.	B.	C.	D.
1	43	40	36	12
2	44	26	19	3
3	126	63	63	46
4	105	47	42	31
5	64	49	35	38
6	107	73	55	38
7	70	66

the American Electrochemical Society has considered the whole question carefully and has recommended a number of tests which are given below.

STANDARD METHODS OF TESTING DRY CELLS.

(As recommended by the Committee* of the American Electrochemical Society.)

SERVICE TESTS RECOMMENDED.

1. *Telephone Service.*—Discharge three cells, connected in series, through 20 ohms resistance for a period of two minutes, each hour, during 24 hours per day and seven days per week, until the closed circuit voltage of the battery at the end of a period of contact falls to 2·8 volts.

The following readings are taken :—

1. Initial open circuit voltage of the battery.
2. Initial closed circuit voltage of the battery.
3. Closed circuit voltage at the end of the first discharged period.
4. Closed circuit voltage at the end of a discharged period after three days, and weekly thereafter.

Report the results as the number of days during which the closed circuit voltage remains above the limiting value of 2·8 volts.

Fig. 158 shows in diagrammatic form a very convenient and inexpensive method of carrying on this test.

The left-hand portion indicates the apparatus necessary and its arrangement. The hand of the clock A revolves once per hour, closing, by means of a suitable contact H, the circuit of the battery I in turn through the contacts B₁, B₂, B₃ and B₄, on the face of the clock. This current magnetises in turn the cores of the relays C₁, C₂, C₃ and C₄, causing the extended armature arms D to fall, bringing the inverted U-shaped fingers

* Consisting of Messrs. C. F. Burgess, J. W. Brown, F. H. Loveridge and C. H. Sharp.

F into mercury cups, to which the terminals of the individual test circuits are connected. Each contact plate B is of such length that two minutes are required for the passage of the contact H.

At the right of the figure is shown one testing unit, consisting of the relay C, the mercury cups into which dip the contact fingers F, and the arrangement of the 20-ohm resistance coils G.

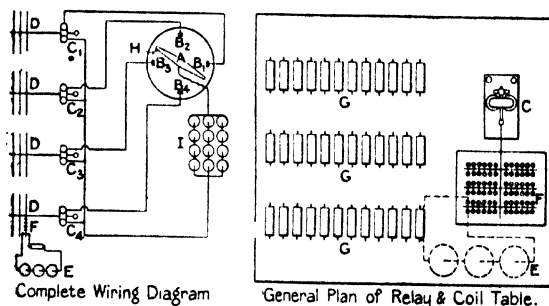


FIG. 158.—Diagram of Arrangement for Telephone Test.

The batteries E are stored under the table on which the various parts are fixed. One complete test battery circuit is indicated by the dotted lines.

Fig. 159 shows a representative discharge curve obtained from a battery of three 2½ in. × 6 in. (6 cm. × 15 cm.) cells of a well known brand. The

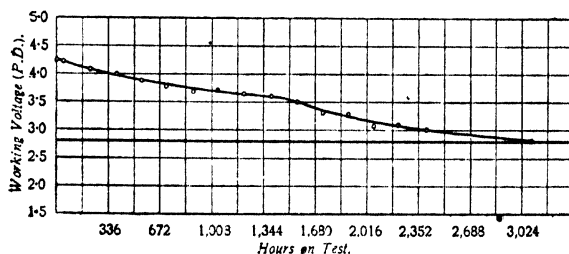


FIG. 159.—Representative Discharge Curve of Cells on Telephone Test.

curve passes through the values of the closed circuit voltage at the ends of the contact periods.

The test should be conducted in a dry place, and normal room temperature should be maintained as closely as possible.

II. Ignition Service.—Discharge six cells connected in series through 16 ohms resistance for two periods of one hour each per day, seven days per week. The periods should be 11 hours apart, but in cases where the circuits are not automatically controlled, the first and the last hour in the working day may be chosen for the discharge periods and the discharge omitted on Sunday, without materially affecting the results.

The following readings are taken :—

1. The initial open circuit voltage and short-circuit current of the battery.
2. The initial closed circuit or working voltage, and the initial impulse of current which the battery is capable of forcing through a 0.5 ohm coil connected in series with an ammeter, and in parallel with the 16 ohm coil.
3. Closed circuit voltage and impulse current through the 0.5 ohm coil at the end of the first period of closure, at the end of the sixth period, at the end of the 12th period, and after every 12th period thereafter.

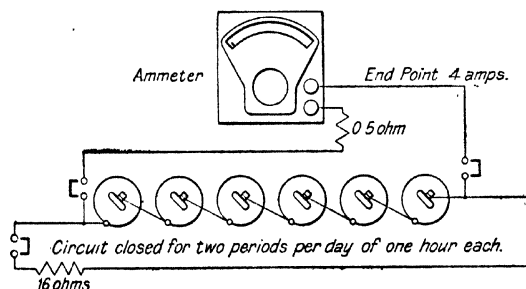


FIG. 160.—Diagram of Arrangement for Ignition Test.

The test is considered completed when the impulse current at the end of a period falls below four amperes. Report the results as the number of hours of actual discharge to the limiting value of impulse current.

Fig. 160 shows diagrammatically the arrangement for a single test.

When the number of tests is not large the circuits may easily be closed by hand. When a great many tests are to be made, it is convenient to arrange a clock-operated automatic circuit closing device.

By varying the length or number of discharge periods, the test may be made representative of any special cases of ignition. For a good comparison of the fitness of various cells for general ignition service, however, the test as given above is to be recommended.

Particular care should be taken to keep the temperature of ignition test batteries as nearly constant as possible, as the service obtainable is

greatly influenced by this factor, as shown by the following Table in which are given the averages of five separate tests conducted at 5, 25, 35, 45, 55, 65 and 75°C. :—

Temperature	5°	25°	35°	45°	55°	65°	75°
Hours service	31.9	46.3	50.4	46.2	35.6	29.3	26.0

The reasons for the adoption of the various constants of this test, viz., number of cells, resistance in main circuit, end point, and resistance in ammeter circuit, is fully described in the "Trans." Amer. Electrochem. Soc., Vol. 13, p. 178 (1908); Vol. 17, p. 361 (1910); and Vol. 19, p. 43 (1911).

III. Flashlight Batteries.—Discharge the battery to be tested through a resistance of four ohms for every cell in series, viz., eight ohms for a two-cell battery and 12 ohms for a three-cell battery, for a period of five minutes once each day until the closed circuit voltage at the end of a discharge period falls to 0.75 volt per cell, viz., 1.5 volts for a two-cell and 2.25 volts for a three-cell battery.

The following readings are taken :—

1. Initial open-circuit voltage and short-circuit current.
2. Initial closed circuit, or working voltage.
3. Closed-circuit voltage at the end of the first, third and seventh periods of closure, and after each seventh period thereafter.

Report the results as the number of minutes during which the battery was discharged through the resistance to the given end point.

In case the circuits are not operated mechanically, the results are not materially changed if the batteries are discharged only on working days.

Four ohms per cell is chosen for the resistance in circuit, since the tungsten bulbs generally used with a three-cell battery have a resistance of approximately 12 ohms.

Miscellaneous Services.—In addition to the telephone and ignition services, which are by far the most important services in which dry cells are used, there are numerous other services, among which may be mentioned the operation of automobile horns, sewing machine motors, small fans, toys, massage vibrators, cigar lighters, bells, buzzers, &c. In the aggregate these miscellaneous services consume enormous numbers of cells, but they are so numerous, and there are such variable conditions prevailing in each kind of service, that it would be useless to attempt to develop standard tests covering them.

It is not difficult for anyone particularly interested in any special service to arrange a suitable test for himself. Care should be taken to make the conditions of test, viz., number of cells, resistance in circuit, period of drain, &c., approximate those of the service in question.

CONSTRUCTION AND TESTS SPECIFIED BY THE BRITISH POST OFFICE.—The general character of the construction required by the British Post Office, and the

tests which the cells must pass, are set out in the following specification :—

GENERAL.

The zinc element of the cell to be preferably formed into a rectangular or cylindrical case having the metal bottom and the sides so connected, mechanically and electrically, that no leakage can take place and the electrical efficiency is not impaired, and to be substantially designed to withstand ordinary transport and handling without damage and with sufficient capacity to retain the contents of the cell without overflow or leakage during its full period of life.

Each cell to be fitted with a stout cardboard cover, bearing the name of the manufacturer, the letters G.P.O., and the index-letter (*see* Table), distinguishing the size of the cell. The cover to be treated with approved insulating compound, to ensure the efficient insulation of the cell from "earth," and the cell so constructed as to be perfectly portable. The overall dimensions of each cell to be in accordance with the Table.

The negative lead to be tinned copper.

The top of the carbon to be fitted with a brass terminal, of approved pattern.

Each cell to be efficiently sealed and ventilated where necessary ; if, for the latter purpose, glass tube be used, it must not project above the surface of the seal.

The cells to be constructed in other respects to the satisfaction of the Engineer-in-Chief to the Post Office or his representative especially as regards suitability of the cells for six months' storage without appreciable local action or deterioration. Six cells of the type which the contractor proposes to supply should be submitted with the tender.

TESTS.

The E.M.F. of the W, X, Y and Z cells, on open circuit, must be not less than 1.5 volts, and that of the P cells not less than 3 volts, and must not fall more than the percentage indicated in the Table below, after the cell has been shunted by a resistance of 2 ohms in the case of the W, X, Y and Z cells, and 4 ohms in the case of the P cells, for a period of 10 minutes.

The resistance must not exceed that specified in the Table for the particular size under test.

Of the cells delivered, 2 per cent., drawn at random, will be tested for "electrical behaviour" by taking out a current of the magnitude specified in the Table for average periods of five hours per day for six days per week until the E.M.F. of the cell falls to 1 volt at the end of the day's period of discharge, or until the resistance rises to a maximum of 3 ohms per cell (except in the case of X cells, where a maximum resistance of 5 ohms will be taken), it being understood that the voltage shall be measured on open circuit, immediately after disconnection. The

minimum output per cell which, under these conditions, will be considered satisfactory for each of the respective sizes of cell, is shown in the following Table.

Table IX.—Post Office Tests.

Index Letter of cell.	Dimensions.				Max. resist. in ohms.	Max. fall of E.M.F. after 10 minutes application of shunt.	Current to be taken out during test.	Min. output in watt- hours.
	Height over all		By					
	Max.	Min.	Max.	Min.				
W.	5½"	5½"	2 1/16"sq.	1 1/16"sq.	0.5	15 per cent.*	20	20
X.	4½"	4½"	1 3/16"sq.	1 1/16"sq.	0.5	20 per cent.*	10	10
Y.	7"	6½"	2 1/16"di.	2 3/8"di.	0.5	10 per cent.*	50	50
Z.	8½"	8"	4 1/16"sq.	4 1/16"sq.	0.25	5 per cent.*	140	140
P.	3½"	3½"	2 7/8" x 1 1/8"	2 1/4" x 1 1/8"	1.0	25 per cent.†	10	12

* With 2 ohm shunt.

† With 4 ohm shunt.

CELLS FOR LABORATORY USE.—Before passing on to the next subject it may not be out of place to say a few words upon cells suitable for use in the laboratory. It is sometimes necessary to have a battery of comparatively high E.M.F., say 100 or 200 volts, from which little or no current is taken—for example, in insulation tests. A cheap method of making such a battery is to mount a number of zinc and copper couples in series in a block of paraffin, which is suspended over a pan of water, the elements of any couple being very close together. Immediately before the battery is required the couples are dipped into the water, of which each couple retains enough to close the internal circuit. This method is simple and convenient, but the internal resistance is very high, and of course increases as the evaporation continues.

The details of such a battery have been worked out by W. S. Tucker.* As shown in Fig. 161 the carbons consist of graphite (blacklead) pencils about 5 cm. long and the zincs are formed from strips of zinc foil about 5 mm. wide, bound to the top of each carbon by wire. After these upper

* *Proceedings*, Phys. Soc., Vol. XXI, p. 640. Manufactured by J. J. Griffin & Sons.

ends have been fixed in a block of paraffin wax (melted for the purpose) the free end of each zinc strip is adjusted close to its corresponding carbon so that the electrolyte will be held by capillary attraction and this spacing is fixed by dipping the

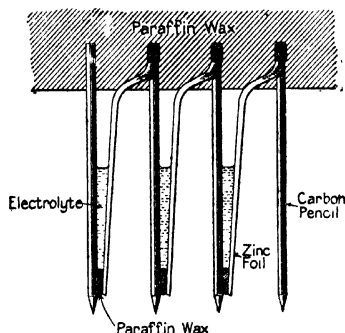


FIG. 161.—Method of Construction of W. S. Tucker's Testing Battery.

ends into melted paraffin wax so that a little wax is taken up as shown. By this means a large number of cells can be arranged in a small space, a tray 18 in. long by 10 in. wide being sufficient for 900 elements.

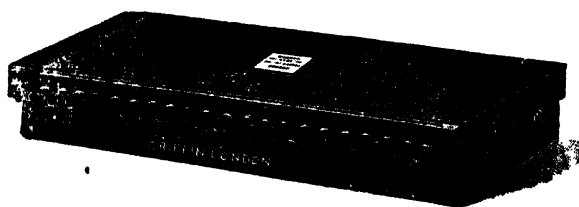


FIG. 162.—Tucker's High-voltage Testing Battery.

The battery is charged by dipping into a solution of calcium chloride, and the strength of the solution is such that it does not tend to increase or diminish in bulk on

exposure to the air, calcium chloride being hygroscopic, unless, of course, the atmospheric conditions change materially. Thus, the battery does not dry up in ordinary use. A voltage of 1.02 volts per cell is obtained and remains constant to within 0.1 per cent. for about two hours and to within 1 per cent. for half a day. One dipping per week is found to be sufficient. It need scarcely be remarked that if any considerable current is taken the polarisation is heavy, but the battery soon recovers. There is no trouble from creeping and less local action than with ammonium chloride. Since all connections are embedded in paraffin

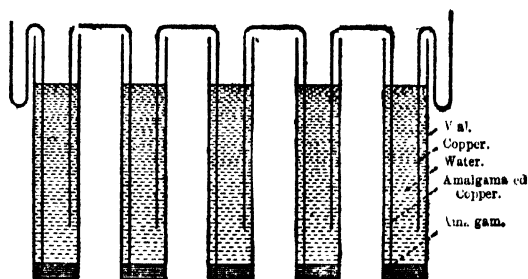


FIG. 163.—Testing Battery.

wax the insulation is easily maintained, and the battery can be readily washed free from electrolyte and stored away when not required.

A. C. Longden* has described a simple form of high voltage battery which he recommends as being satisfactory. The cells are set up in small homœopathic vials. The plates consist simply of bent copper strip as indicated in Fig. 163, the two ends of any strip dipping into adjacent vials and being unequal in length.

* *Electrical World*, Vol. XXXI., p. 681, 1906.

The longer end of each strip is amalgamated with mercury containing a little zinc. At the bottom of each vial is placed a little zinc amalgam into which dips the longer part of the copper strip. Water, to which 1 per cent. of sulphuric acid has been added, is used as the electrolyte. Whereas zinc in such a cell would deteriorate rapidly through local action, the amalgamated copper is satisfactory and is kept in good condition by the zinc amalgam. The top of each pair of plates should be coated with paraffin or shellac to prevent creeping of mercury or salts. The internal resistance of a cell is stated to be about 60 ohms if the vial is 7 cm. \times 1.7 cm., and 2,000 ohms if the vial is 3.5 cm. \times 0.7 cm.

If a larger current is required, small dry cells or silver chloride cells may be used. The former, however, tend to dry up and the latter are troublesome. A battery of very small accumulators is more convenient if there are means for charging.

A small current, if required for a long time, is best obtained from a gravity Daniell cell.

The Grove cell is satisfactory if a heavy current is required for a short time, say, for four or five hours, and the same remark applies to the Bunsen cell, though it is more variable. The bichromate cell will also supply a heavy current, but it is far from constant. It has the advantage, however, that, being a one-fluid cell, it may be allowed to rest without being dismantled, except that the zinc should be removed.

Probably the most serviceable cell for all-round work in the laboratory is some form of copper oxide cell. It has the great advantage that it may be allowed to rest without being dismantled. The local action is generally negligible and the internal resistance is small. But unfortunately the E.M.F. is low, which increases the cost of a cell that in any case is expensive.

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CHAPTER XL

STANDARD CELLS.

Conditions to be fulfilled by Standard Cells, p. 319.—Board of Trade Clark Cell, p. 320.—Preparation of Materials, p. 322.—Permanence of the Board of Trade form, p. 328.—Sources of Error in the Board of Trade form, p. 329.—Kahle's H-form, p. 330.—Temperature Coefficient and Lag, p. 337.—Portable Clark Cells, p. 341.—Other Forms of Clark Cell, p. 345.—The Weston, or Cadmium, Cell, p. 346.—Methods used at the National Physical Laboratory, p. 349.—Methods used at the Bureau of Standards, p. 353.—Electrolytic Methods of Preparing Mercurous Sulphate, p. 354.—Size of Grain of the Mercurous Sulphate, p. 357.—The Form of Cell, p. 358.—Portability, p. 361.—E.M.F. of H and Board of Trade Types, p. 363.—Effect of Composition of the Amalgam, p. 363.—Temperature Coefficient and Lag, p. 367.—Hysteresis, p. 368.—Reproducibility, p. 369.—Constants of Standard Cells, p. 370.—Standard Cells in Electrical Measurements, p. 371.—Helmholtz Cell, p. 374.—Bibliography, p. 375.

In electrical measurements the three quantities which are most frequently determined are resistance, current and electrical pressure. These are very simply related by the well-known law of Ohm, and consequently, if any two of these quantities have been determined for any circuit to which this law applies, the third is readily deduced. In order to carry out such measurements certain instruments are required and standards are necessary for reference. The legal English standards for these quantities are three instruments which are kept in the laboratory of the Board of Trade in Westminster. These standards were rendered legal by an Order in Council on the 23rd of August, 1894,* and are

* Superseded in 1910 by the Order in Council of January 10th of that year.

of value for the purpose of checking the accuracy of other instruments of a similar kind. They are not in any sense arbitrary standards, for they depend upon certain properties which have been carefully determined at intervals. Thus, in the preamble to the Order in Council of 1910, it is stated that the ohm is equal to 10^9 C.G.S. units, and is represented by the resistance offered to an unvarying electric current by a column of mercury, at the temperature of melting ice, 14.4521 grammes in mass, of a constant cross-sectional area and of a length 106.300 cm. The standard ohm is a wire which has been carefully adjusted to the resistance of an ohm as above defined. Similarly, the ampere has one-tenth the value of the C.G.S. unit, and is represented by the unvarying electric current which deposits silver, under certain conditions, in a silver volt-meter at the rate of 1.11800 milligrammes per second.

From the above it is seen that the practical units called the ohm, the ampere and the volt are defined in terms of the C.G.S. units. Of the relations between the practical and the C.G.S. units there can be no question, as it is a matter of definition. But the values of the practical units in terms of the properties of certain bodies, although definite, are not fixed, because they are the results of experience and investigation. For example, the practical definition of the ohm depends upon our knowledge of the specific resistance of mercury expressed in C.G.S. units. The value of this resistance does not change; but as our knowledge of its value becomes more and more extended the results of past investigation have to give way to those of more recent determinations. Hence it is that the expression of the ohm in terms of the resistance of a column of mercury has been changed from time to time, and there are a corresponding number of ohms; for example, the B.A. ohm, the legal ohm (1884), the "true" ohm and the "international" ohm (1894 and 1908). These various

units merely indicate that the state of our knowledge has changed.

In 1908 the International Conference of Electrical Units and Standards, held in London, adopted the arbitrary figures of 106.300 cm. as the length of the mercury column and 0.00111800 gramme as the electrochemical equivalent of silver; not that these figures are absolutely correct, but they are very near the truth, and it is confusing for practical purposes to have such quantities changed from time to time.

The Order in Council of 1894 gave a legal status to the Clark cell as a standard of electrical pressure. No mention, however, is made of standard cells in the Order of 1910, and consequently they have no legal standing, though largely used, at the present day.

CONDITIONS TO BE FULFILLED.—A voltaic cell is a very convenient standard of E.M.F., provided certain conditions can be fulfilled. These may be summed up as follows:— (1) The cell should be readily reproducible, *i.e.*, the E.M.F. should be the same, within certain limits, when the cell is set up by different people using chemicals from different sources. (2) The E.M.F. should preferably not change with age. (3) If the E.M.F. changes with the temperature the change should be definite, and the E.M.F. should have a constant value at any given temperature. This condition applies to physical changes in general. (4) The cell should be portable if possible.

These conditions are difficult to fulfil, and therefore a great deal of investigation has been necessary in order to find a cell which is really satisfactory. The silver chloride or De la Rue cell was at one time suggested as a standard. Raoult* and Lodge† attempted to use the Daniell cell. Fleming‡ after a careful investigation, introduced a special

* *Ann. de Chim. et de Phys.*, 4th series, Vol. II., p. 334, 1864.

† *Phil. Mag.*, 5th series, Vol. V., p. 1, 1878.

‡ *Phil. Mag.*, 5th series, Vol. XX., p. 126, 1885.

form of Daniell cell as a standard, but it was troublesome to set up, and was wanting in portability and permanence. The first really successful standard was that introduced by Latimer Clark* in 1873, which is known as the Clark cell, and which, after certain modifications as to the treatment of the materials, was finally given a semi-legal position in this country, as already stated.

THE CLARK CELL.

THE BOARD OF TRADE CLARK CELL.—The cell referred to in the preamble to the Order in Council of 1894 is generally known as the Board of Trade cell, or more briefly as the B.T. cell. The method of construction was given in detail at the same time in a specification, which was reproduced in full in the first edition of this work. At the present time, however, the Board of Trade cell has entirely lost its importance, and therefore we shall only describe it briefly.

The cell is shown in section in Fig. 164. It is conveniently set up in a "sample tube." The electro-negative element is mercury, and contact with this is obtained by a platinum wire sealed into a small glass tube. Above the mercury is a paste made up of mercurous sulphate, crystals of zinc sulphate, saturated zinc sulphate solution and a little mercury. The mercurous sulphate acts as a depolariser and the zinc sulphate as the electrolyte. The electro-positive element is a zinc rod. A piece of cork is used to carry the zinc and the glass tube protecting the platinum terminal, and the cell is completed by sealing with marine glue, which may be rendered more permanent by coating with sodium silicate solution.

All the constituents should be pure. If the zinc sulphate is acid, the crystals should be dissolved and zinc oxide

* *Phil. Trans.*, Vol. CLXIV., p. 1, 1874; *Journal Soc. Tel. Eng.*, Vol. VII., p. 83, 1878.

added to the extent of 2 per cent. of the weight of the crystals. The solution is then warmed, but not above 30°C ., and when it is free from acid some mercurous sulphate is added, to the extent of about 12 per cent. of the crystals. The solution is filtered while still warm, and, if properly carried out, crystals form on cooling. The paste is formed by adding saturated zinc sulphate solution, as above prepared, to washed mercurous sulphate, adding also zinc sulphate crystals from the stock solution and a little mer-

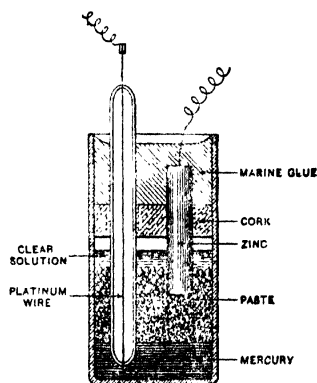


FIG. 164.—Board of Trade Clark Cell (full size).

cury. These are shaken together to form a paste of the consistency of cream, and this is heated to a temperature not exceeding 30°C . for an hour, the paste being agitated from time to time. Crystals should then be visible throughout the mass. In setting up the cell, the platinum wire is heated red hot to clean it, and is then placed in the mercury; the whole of the wire protruding from the glass tube must be below the surface of the mercury. The cork, after being suitably bored to take the tube and the zinc, and

nicked so as to allow air to escape when being inserted, is washed thoroughly in warm water and left to soak for some hours before use. It is then dried. After the paste has been put into the cell the zinc is placed in position in the cork, which is then threaded on to the tube containing the other terminal, and pressed down into position. Such, briefly, is the method of setting up the Board of Trade Clark cell. The E.M.F. of such a cell should be 1.433 volts at 15°C.

It will be realised that the essential constituents of the Clark cell are mercury, mercurous sulphate, zinc sulphate and zinc (or its equivalent in zinc amalgam). These may be varied in the form in which they are put together and in the methods by which they are prepared.

The Board of Trade form of cell did not prove satisfactory in practice, more particularly from the point of view of permanency. Other methods have, therefore, been developed for preparing the materials, and the tube form has been generally discarded in favour of the **H**-form.

NOTES ON THE PREPARATION OF MATERIALS.—

In regard to the preparation of materials, the reader should refer to the methods followed by Kahle (given on a later page) and those described in connection with the Weston cell. The following general notes, however, may prove useful, as being introductory to these specialised methods.

The Mercury.—The purity of the mercury is a matter of great importance, it being essential that there should be no electro-positive impurities present, such as zinc. It is generally possible to purchase re-distilled mercury which is sufficiently pure for the purpose, but it is sometimes preferable to carry out the necessary purification.

The usual method of purification is by distillation *in vacuo*. Before this is effected, the mercury may be agitated

with dilute nitric acid to remove the oxide. If reddish brown fumes appear during this treatment the acid is too strong, and should be diluted. After shaking for some time, the mercury is washed by decantation until free from acid, and is dried as far as possible by means of blotting paper. This drying may be conveniently completed by allowing the mercury to flow through a filter paper which has been perforated with a very small hole and is held in a funnel. When mercury has been used in a laboratory, impurities such as zinc and cadmium are common, and these are not readily removed by distillation. In such case, the mercury is electrolysed before distillation. The mercury is made the anode in a 2 per cent. nitric acid solution, a piece of platinum foil being used as a cathode. The more electro-positive metals go into solution, leaving in the mercury those of a less positive nature, which are afterwards removed by distillation. Details of this method are given later.

To avoid the distillation of impurities and the formation of oxide, the mercury must be distilled *in vacuo*. For this purpose a number of stills have been devised, some of which are automatic in the production of a vacuum and in the supply of mercury, while others require the application of an air pump before they can be operated. If an air pump is at hand, and only a small quantity of mercury is required, it is simplest to make use of an ordinary glass retort to which a receiver has been fitted so that it can be exhausted. The receiver should also be in communication with a vessel containing concentrated sulphuric acid, as a good vacuum will otherwise be unobtainable. A few steel turnings may be placed in the retort to prevent bumping, but this is usually unnecessary. If the pressure is less than 2 mm. of mercury, the distillation goes on with ease and rapidity.

Some chemists object to distillation on the ground that

certain impurities are sufficiently volatile to pass over into the receiver. For this reason distillation is sometimes carried out in a stream of air under reduced pressure, so as to oxidise such impurities. Other methods, which also have the advantage of greater simplicity, are occasionally employed. For example, after the mercury has been shaken up with dilute nitric acid, or acid mercurous nitrate, and subsequently washed and dried as already described, it may be subjected to either of the two following modes of treatment: (1) The mercury is shaken with a coarse powder, such as sugar or sand, thus causing a large surface to be exposed to the air, with consequent oxidation and removal of impurities. (2) A stream of air is forced or aspirated through a long column of the mercury for a considerable time. In either case a good deal of dross is formed which contains most of the impurities and is removed by allowing the mercury to flow through a perforated filter paper, or, preferably, by forcing it through clean wash-leather. The Author has not had personal experience of these methods, but they are said to give very good results.

The Zinc.—This is generally obtainable of sufficient purity.

The Mercurous Sulphate.—The experiments of Rayleigh indicate that the mercurous sulphate serves to maintain the purity of the mercury and to produce greater steadiness of the E.M.F. It also plays the part of a depolariser.

As pointed out by Swinburne, pure mercurous sulphate may be obtained by adding an excess of zinc sulphate to a solution of mercurous nitrate, both of which reagents are easily obtainable in a pure condition. After removing the zinc nitrate which is formed, the mercurous salt is ready for use, but as it is then moist a large excess of zinc sulphate crystals must be added in making up the paste.* Many other methods have been used, as detailed later.

* Brit. Assoc. Report, 1884, p. 651, and *Phil. Trans.*, Vol. CLXXVI., A. 781, 1885.

Mercurous sulphate, as purchased, varies considerably in colour, according to its state of purity. A grey colour probably indicates the presence of free mercury, which is not objectionable. A yellow colour is due to basic salts, which should be avoided. The most serious impurity is mercuric sulphate, which breaks up in the presence of water into acid and a yellow basic sulphate, called turpeth mineral. Even mercurous sulphate undergoes hydrolysis in the presence of water, and consequently washing with water as a means of purification has now been abandoned. The mercurous sulphate is the ingredient which has given the most trouble in arriving at a satisfactory result.

The Zinc Sulphate.—Impurities in the zinc sulphate may have a considerable effect upon the E.M.F. The salt should be tested for iron, preferably by adding a drop of ammonium sulphide, which gives a perfectly white precipitate if no iron is present. Potassium thiocyanate gives a red colour if the salt contains iron in the ferric state. Iron may be removed by Kahle's method, which is described on page 332, but it will be found far simpler to purchase sulphate which is free from this impurity. Fortunately, crystallisation provides an easy means of purification, and electrolysis has also been used for this purpose.

The object in keeping to a temperature below 30°C. is to obtain crystals having the formula $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, i.e., with seven molecules of water of crystallisation. If crystals form at a higher temperature than 39°C., a lower hydrate is formed and the E.M.F. is affected. Clark cells should not be employed at a higher temperature than 35°C.

Free zinc oxide in the final solution is objectionable because it would react with the mercurous sulphate which is added in making up the paste, zinc sulphate and mercurous oxide being formed. The latter might be deposited on the zinc and affect the E.M.F. Consequently, in the

Board of Trade instructions, sufficient mercurous sulphate is added in the preparation of the zinc sulphate to combine with all the zinc oxide originally added to the solution.

At the National Physical Laboratory, purchased zinc sulphate is dissolved in hot water, and a slight excess of pure zinc oxide, together with a little hydrogen peroxide, is added. The peroxide assists the oxidation of any iron salts to the ferric state. The mixture is heated on a water bath (heated electrically to avoid the possibility of zinc sulphide being formed from gas fumes) for four hours. It is then filtered and made acid to the extent of about 2 parts in 10,000 with sulphuric acid. A mixture of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ (the latter forming at 39°C .) is then separated by evaporation of the solution at 100°C ., and subsequent cooling by a freezing mixture. The crystals so obtained are washed twice with distilled water and then dissolved to form a practically saturated solution, from which zinc sulphate crystals are obtained by slow evaporation at room temperature. A second re-crystallisation gives crystals suitable for standard cells.

Progress of the neutralisation may be tested by means of litmus paper, of which the red colouration will be observed to become less and less marked as time goes on; but after four or five hours it will cease to diminish further. The dull port wine colour that continues cannot be diminished, as it does not indicate the presence of acid, but is due to the inherent acidity of zinc sulphate which cannot be removed.

Setting up a Tube Cell.—The platinum should be sealed into the glass protecting tube by means of enamel, which is sold in sticks for this purpose by practical glass blowers. White enamel is generally unsuitable for this work, the pink or blue coloured enamel being preferable. Unless the platinum wire is surrounded by enamel the glass is liable to crack on cooling. Lead glass is free from this difficulty,

but it blackens unless it is worked at the extreme end of the blowpipe flame. The platinum wire is allowed to extend about half an inch beyond the glass at either end, and a copper terminal wire is soldered to one end.

The paste is most conveniently introduced into the cell by means of a dry funnel, great care being taken that the paste does not touch the upper part of the tube. If the sides of the tube above the cork become soiled by the paste, the liquid in the cell rises by capillary action between the glue and the glass, and may damage the seal.

While the paste is being introduced the platinum should be kept in position so that it does not rise out of the mercury. When this operation is complete, the cork, with the zinc in position, is passed over the glass tubing containing the platinum, which is still kept in place, and pushed down until it is nearly in contact with the paste. The corks are more easily handled if they are not completely dried; removal of the adherent water by means of filter paper will be found sufficient.

It is preferable to have the zincs in all cells dipping to the same extent into the paste, and all passing into the crystals which collect on the surface of the paste, not merely into the clear solution. It appears that contact between the actual paste and the zinc may give rise to unsteadiness if the cell is shaken, owing to fresh parts of the zinc coming into contact with the paste; but the zinc should at least dip into the crystals covering the paste. A saturated solution containing crystals is not necessarily saturated at the top; and therefore, if the zinc dips merely into the solution, the E.M.F. may be due to an unsaturated solution, and may differ from the E.M.F. of a cell in which the zinc passes into the crystals.

Undue heating of the cells by the melted marine glue used in the sealing may be avoided by standing them in

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SOURCES OF ERROR IN THE BOARD OF TRADE

CLARK CELL.—Both the construction of the cell and the preparation of the materials are open to a good deal of criticism. The chief objection to the method of construction lies in the position of the zinc. This may dip merely into clear solution, or it may pass into the layer of crystals which collect on the top of the paste, or it may pass into the paste itself. The position is not clearly

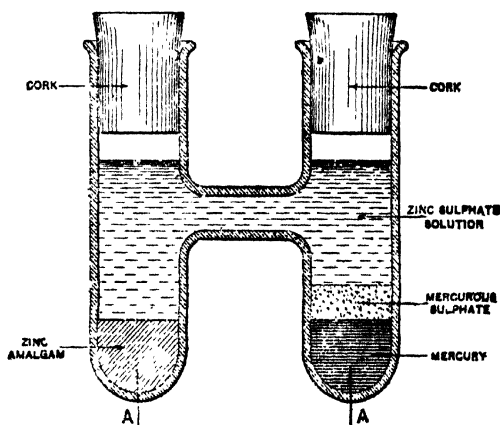


FIG. 165.—Rayleigh's H-form of Clark Cell.

defined in the specification. If it tips only into the solution it may really be in contact with solution that is unsaturated, as already explained. If it passes into the crystals or into the paste it may then be partly in saturated and partly in unsaturated solution, and local action may occur. The conditions, therefore, are not very definite. The best known form of cell in which this defect is remedied

is the **H**-form, due to Rayleigh.* This consists of two small test tubes connected by a cross tube as shown in section in Fig. 165. A platinum wire, A, is sealed into the bottom of each tube, one making contact with mercury, and the other with the zinc amalgam. Above the mercury is a layer of mercurous sulphate. The cell is filled with a saturated solution of zinc sulphate above the level of the cross tube, a few crystals being also added, and the test tubes are closed with indiarubber corks. In this cell voltaic action can take place only at horizontal surfaces of mercury or amalgam, which are in contact with saturated solution. The result is therefore definite. This arrangement of the constituents of a cell appears to be of considerable importance, and it is probable that unsatisfactory results are liable to be obtained in the Board of Trade form even if the materials are satisfactorily prepared. In fact, the Author has found that cells set up in the Board of Trade form, but with materials which had been prepared according to Kahle's method (described hereafter), and which had given excellent results in **H**-form cells, were far from satisfactory at the end of six years.

Apart from the form of the Board of Trade cell, the methods of preparing the materials are not sufficiently definite to ensure the best results.

We will now pass on to a description of Kahle's cell, and his method of preparation, in which these defects have been removed.

KAHLE'S H-FORM OF OLARK CELL.—The form of cell used by Kahle is illustrated in Fig. 166. It only differs from Rayleigh's form in that the cross tube is rendered unnecessary by uniting the two side-tubes at the top.

* *Phil. Trans.*, Vol. CLXXV., Part 2, pp. 411-460, 1884.

The construction of the cell and the preparation of the materials are described by Kahle* as follows :

Construction of the Cell.

The vessel used for the cell consists, as shown in the figure, of two vertical branches closed at the bottom, and joined at the top into a neck closed by a ground-glass stopper. The diameter of the branches should be at least 2cm., and their length 3cm. The neck of the vessel should be 1.5cm. wide, and at least 2cm. long. Platinum wires about 0.4mm. thick are fused into the bottom of both branches.

The vessel is filled in a manner depending upon whether the cell is to be used at the place of construction or is to be transported.

In the former case pure mercury is poured into one branch, and into the other an amalgam of about 90 parts of mercury and 10 parts of zinc, which is fluid when hot and solidifies on cooling. The platinum wires must be completely covered by the mercury and the amalgam respectively. Upon the mercury is poured a layer of paste 1cm. deep, made by rubbing together mercurous sulphate, mercury, zinc sulphate crystals, and concentrated solution of zinc sulphate. This paste and the amalgam are then both covered with a layer 1cm. deep of zinc sulphate crystals, and finally the whole vessel is filled with concentrated zinc sulphate solution until the stopper on being introduced just touches the surface. Care should, however, be taken that the vessel contains a small air-bubble, since that prevents its bursting in the case of a great rise of temperature. At the final closing of the vessel the glass-stopper is brushed over at its upper edge with shellac dissolved in alcohol and then firmly inserted.

If the cell is to be sent away, a circular electrolytically-amalgamated piece of platinum foil, about 1cm. across and 0.1mm. thick, takes the place of the mercury, and is firmly attached to the platinum wire introduced through the bottom. Zinc amalgam forms, as before, the negative electrode, and is covered with a layer of zinc sulphate crystals 1cm. deep. The rest of the vessel is filled up to the stopper with mercurous sulphate paste. The final closing is effected as already described.

Preparation of the Materials to be used in the Cell.

Mercury.—All mercury to be used in the cell should be purified by the ordinary processes, and distilled in vacuo.

Zinc.—The commercial pure zinc may be used without treatment. To prepare the amalgam, add one part of zinc to nine parts

* *Zeitschrift für Instrumentenkunde*, 1893; *The Electrician*, Vol. XXXI., p. 265, July 7, 1893.

of mercury, and keep both in a porcelain dish at 100 deg., stirring gently till the zinc is completely dissolved in the mercury.

Zinc Sulphate.—Before use test the commercial zinc sulphate for acid with litmus and for iron with potassium sulpho-cyanide. If it is sufficiently pure it may be at once re-crystallised in the way detailed below. If it contains appreciable traces of free acid, equal parts of the zinc sulphate and distilled water are boiled with zinc filings in a suitable porcelain dish until no further gas is given off at the zinc, and the solution shows after cooling a white, or, in the presence of a ferric hydrate, a brownish precipitate of zinc hydrate. If the solution is free from iron it may be filtered off after standing for two days. Otherwise it is again heated to 60 or 80 deg., and electrolysed for six hours with a current not exceeding 0.2 ampere, the electrodes being two pieces of platinum foil of about 50 sq. cm. surface suspended in the liquid. The liquid having cooled over night, litmus is again employed to test whether any acid has been formed during electrolysis. In that case the boiling with zinc filings must be repeated, and the solution again electrolysed by weak currents. It is therefore well to cover the vessel containing the solution with a glass plate, so that but little water vapour can escape. As soon as the solution is sufficiently free from acid and iron it is filtered off. To each litre of the filtrate about 50 gm. of mercurous sulphate, free from acid, are added and well stirred. The mercury salt will in general assume a yellow colour after long standing. If the solution has stood for a day, and a portion of it, on being shaken up with more mercurous sulphate, does not turn perceptibly yellow, the solution may be filtered off and concentrated in a flat porcelain dish over a water bath. Here care must be taken that the crystals do not form at too high a temperature, as otherwise they easily lose a portion of their water of crystallisation. To secure this the flame under the water bath is extinguished, and the dish left in position covered with a glass plate. If after further cooling no crystals are separated, further concentration is necessary. If the heating was too protracted, and the crystals were formed under unfavourable conditions, a little water must be added and the whole warmed until everything is re-dissolved. The concentrated solution is poured off, and either further evaporated or kept for further use. The last traces of the solution are removed from the crystals by letting the dish stand for some time in a slanting position. It is not advisable to sharply dry the crystals, as they thereby lose water of crystallisation. For the same reason they must be kept in a closed vessel.

Mercurous Sulphate.—The mercurous sulphate used must not be coloured yellow by basic salt. If that should be the case, stir up

one part of the salt with two parts of distilled water, and add, with constant stirring, so much of a solution of one part of sulphuric acid to 1,000 parts of water as is necessary to make the colour disappear. Then pour off the liquid and wash the paste several times with distilled water, but without thereby causing another yellow colouration. If the sulphate is white to begin with, and only shows a faint yellow colouration after considerable time on shaking up with distilled water, it may be used at once. If this colouration is not shown on shaking up with water, the salt must be washed several times with distilled water until the first traces of yellow colouration appear. If it has been necessary to wash the salt, the water should be driven off as much as possible by mechanical means. If dried by heat the yellow colouration will re-appear. In order to avoid keeping moist salt, only so much of it should be treated by the above process as is necessary for the purpose in hand.

To prepare the paste, two parts of the sulphate should be added to one part of mercury. If the sulphate is dry, it should be stirred up into a paste with zinc sulphate crystals and concentrated zinc sulphate solution until the whole forms a stiff mass everywhere permeated by zinc sulphate crystals and small globules of mercury. But if the sulphate is wet, only zinc sulphate crystals should be added, taking care, however, that they are in excess, and are not dissolved even after prolonged standing. Here, also, the mercury must permeate the paste in small globules. It is well to crush the zinc sulphate crystals a little before using, so that the paste may be more easily manipulated later on.

Details of Construction.

For the preparation of cells containing mercury as the positive electrode, the following details should be attended to: Before introducing the hot zinc amalgam place the glass vessel, well cleaned and carefully dried, into a hot-water bath. Then pass a suitable thin-walled glass tube through the neck of the vessel on to the bottom of the branch which is to contain the amalgam. The tube ought to be as wide as is consistent with the dimensions of the vessel. It is intended to protect the rest of the vessel from contamination. The amalgam is introduced by means of a glass tube about 10cm. long drawn out into a point, the other end being provided with an indiarubber tube about 3cm. long closed by a short glass rod. The point of the tube is inserted below the surface of the liquid amalgam heated in a dish, and a portion of the amalgam is sucked into the tube by compressing and releasing the indiarubber. The point is then quickly freed from external impurities derived from the surface of the amalgam, introduced

into the cell through the wide tube, and emptied by pressure on the indiarubber. The point ought to be so fine that the amalgam does not issue except on pressing the rubber. The process is continued until the branch contains the required quantity of amalgam. The vessel is then taken out of the water bath. After cooling, the amalgam should adhere firmly to the bottom of the vessel and exhibit a bright metallic surface.

To introduce the mercury and the paste a suitable funnel with a long tube is used. The paste should not touch the upper walls of the vessel, but may be pushed in with a glass rod if too stiff to flow.

Before pouring in the zinc sulphate solution, the paste and the zinc amalgam should be covered with zinc sulphate crystals, as these prevent a creeping up of the paste after wetting with the solution. In filling, the zinc sulphate crystals and the paste should not contain large air-bubbles. These may be removed by knocking.

Kahle lays stress upon the fact that the mercury should be free from any electro-positive metals, that zinc sulphate crystals should be always present in excess, and that the solution should contain no free acid.

The boiling of the zinc sulphate solution with zinc filings (which should be tested for iron) is most conveniently carried out in a flask which is fitted with a cork and a vertical open glass tube about 3 ft. in length; the latter acts as a condenser, returning the condensed steam to the flask, and keeps the solution of the same strength throughout the operation. It is not easy to see when bubbles of hydrogen cease to be evolved, as mentioned in the instructions, but it will be found sufficient to boil for three or four hours. At the end of that time a precipitate of zinc hydroxide forms on cooling, showing that no free acid is present.

The crystallisation of the zinc sulphate is a little troublesome to carry out successfully when one is unaccustomed to the process. The Author has found it best to stop the evaporation as soon as a decided incrustation begins to form on the dish at the edge of the liquid. When that is so the dish should be covered with a clock glass and allowed

to cool slowly. With a little practice a good yield of the required crystals can be obtained without fail, but it is generally advisable to determine the amount of water of crystallisation in order to be certain that the crystals are sufficiently hydrated.

Kahle states that cells set up according to his method seldom differ in E.M.F. by so much as 0.0001 volt, i.e., by

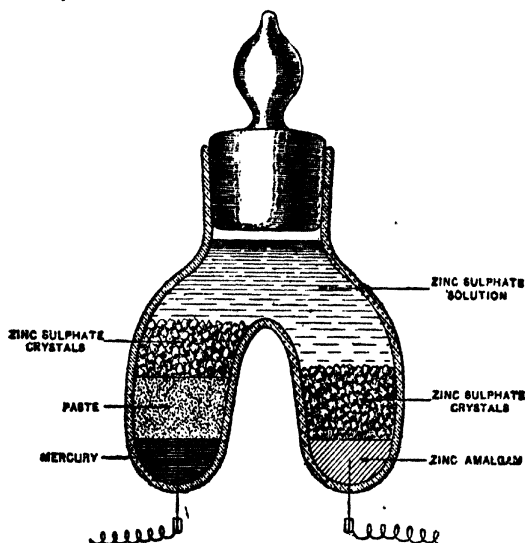


FIG. 166.—Kahle's H-form of Clark Cell (full size).

one part in 14,000. The accuracy is therefore very much greater than in the case of the Board of Trade cell. The permanency also appears to be far more satisfactory. Of four cells which the Author set up, the difference, after six and a-half years, of any one of them from the mean value of the four cells was seldom greater than 0.0001 volt, and the mean arithmetical difference did not exceed 0.00005 volt.

About 15 years later the differences from the mean value varied from less than 0.0001 volt to 0.0007 volt, and the mean arithmetical difference was about 0.0003 volt.

The only objection to Kahle's cell is that it is not very simple in its construction and in the preparation of the materials. In common with all H-form cells, it has the disadvantage that it cannot be placed in a water bath;

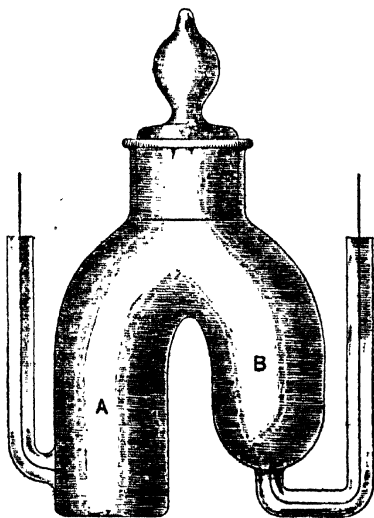


FIG. 167.—H-form Cell modified for use in a Water Bath.

oil must be used, which is less convenient, and a more or less complicated stand must be made to support it. If the glass stopper carries a thermometer dipping into the solution, as used by Kahle, then, of course, a bath is unnecessary for the observation of temperature; but such a thermometer increases the cost and can only give approximate indications owing to its shortness and the smallness

of the graduations. It is therefore simpler, and really as effective, to make cells with a plain stopper, as shown in Fig. 166.

Fig. 167 shows a modified H-form cell devised by the Author to overcome this inconvenience. The platinum wires are sealed in and brought up through small glass tubes which protect them from the bath. The limb A is made with a square end, so that the cell can stand without support, and contains the mercury, while the limb B is made with a rounded end, as the amalgam is liable to crack the tube if made otherwise. The difficulty may also be overcome by using internal wire terminals, as mentioned later in describing the Weston cell.

The Rayleigh H form of Clark cell is now generally adopted in Great Britain and the United States. The observations of G. A. Hulett and F. A. Wolff, in America, and of F. E. Smith, at the National Physical Laboratory, show that when the materials are prepared with care Clark cells are as reproducible and as constant as Weston cells.

TEMPERATURE COEFFICIENT AND LAG.—Since 15°C. is regarded as a normal mean temperature, the value of the E.M.F., E , of a cell at any temperature, t , is generally expressed in the form of an equation as follows :

$$E_t = E_{15} \{1 + a(15 - t) + b(15 - t)^2\},$$

in which E_{15} is the value of the E.M.F. at 15 deg., and a , b are constants. The last term is always very small, and may be neglected in all ordinary measurements, in which case a is known as the temperature coefficient. It is very generally assumed that this coefficient for the Clark cell is 0.08 per cent., or, in other words, that the E.M.F. falls 0.0011 volt for every degree Centigrade rise in temperature.

In experimental work involving the use of the Clark cell, temperature corrections have to be frequently intro-

duced owing to the high value of the temperature coefficient. In order to avoid such corrections, A. Campbell* has suggested an automatic compensator which consists of a Leclanché cell and four resistances of two different materials. The latter are so arranged that, on account of their different temperature coefficients, the necessary E.M.F. is added to, or subtracted from, that of the standard cell, thus eliminating the correction.

The accepted value of the temperature coefficient is the result of a number of observations by different observers on cells which were carefully maintained at various temperatures for a considerable time. In practice, however, the temperature is always changing to some extent, and it therefore becomes a matter of some importance to determine how quickly the E.M.F. of a cell follows variations in temperature. These changes depend not merely upon the equalisation of temperature, but more particularly upon the varying solubility of the zinc sulphate, upon diffusion, upon solution and re-crystallisation. Changes in the E.M.F. would, therefore, be expected to lag behind those of temperature.

To investigate the question of lag, Prof. Ayrton and the present Author† submitted Board of Trade cells to cyclical changes of temperature through 8 or 10 deg. at a constant rate. The temperature was first raised and then lowered, or vice versa, the cell being brought back to the initial temperature at the end of the experiment. It was found that cells respond very readily to changes in temperature, even changes of 0.1 deg. being often quickly noticeable. But it was observed that the full change did not, as a rule, take place until after the lapse of a considerable time, and that a cell generally failed to give its initial E.M.F. when the cycle was completed. In Fig. 168, curve A

* *Phil. Mag.*, Vol. XLV., p. 274, 1898.

† *Proc. Roy. Soc.*, Vol. LIX., p. 368, 1895.

shows the result obtained in one of the experiments, in which the cell was subjected to a fall and a subsequent rise of temperature at a practically uniform rate of 1 deg. in

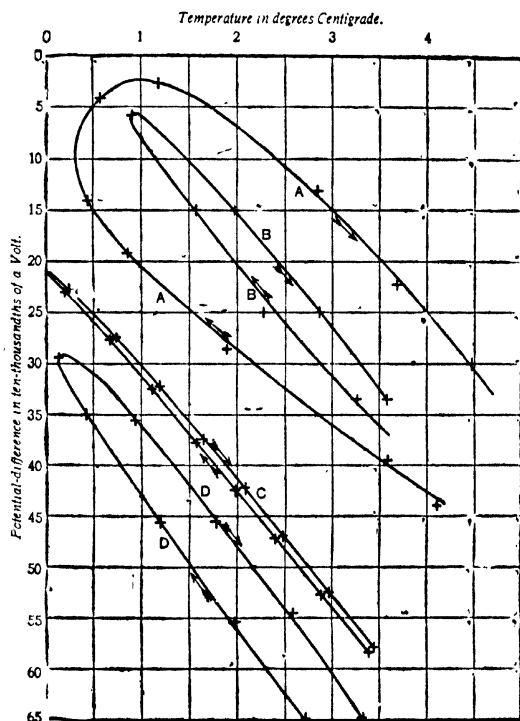


FIG. 168.—Curves showing the lag in H-form Cells as compared with Board of Trade Cells.

- | | |
|---|---|
| A. An average curve for B.T. Cell. Rate of change of temperature, 1 deg. in 15 min. (from Ayrton and Cooper's Paper). | B. H-form, 1 deg. in 15 min.
C. " 1 deg. in 30 min.
D. " 1 deg. in 7 min. |
|---|---|

15 minutes. This curve shows the connection between E.M.F. differences (from the standard) and the temperature,

and is seen to be a more or less closed curve, the enclosed area being due simply to lag. In some cases the curve is closed, but generally that is not so, and the cell acts as if its E.M.F. were raised or lowered by a small amount depending upon the direction in which the temperature has been raised. It is probable, however, that the cells would regain their initial condition by the following day, and that the curves would all be closed if the observations were continued long enough. It thus appears that there is always what may be called a "simple lag," which may be removed by a comparatively short interval of constant temperature, and there is also often what may be termed a "semi-permanent lag," which varies in amount and requires many hours of steady temperature for its complete removal. On account of the pronounced character of the lag in the Board of Trade form of cell the effective temperature coefficient is liable to be somewhat smaller than the accepted value.

Callendar and Barnes* have given records illustrating the slowness with which the E.M.F. may follow a sudden rise of temperature under certain conditions. Two cells of the Board of Trade type, exactly similar, were taken from a constant temperature bath at 14°C. and placed in a second bath at 25°C. After two days one of the cells was shaken occasionally, and rapidly gained the correct value of the E.M.F., but the other cell, which was left undisturbed, required nearly a fortnight before the normal value was assumed.

If the zinc dips only into the clear solution the temperature coefficient appears to have about half the accepted value. Carhart† has advocated this method of construction as a means of reducing the temperature coefficient, and he states that the E.M.F. is thereby raised 0.4 per cent.

* *Proc. Roy. Soc.*, Vol. LXII., p. 117, 1897.

† *Phil. Mag.*, Vol. XXVIII., p. 420, 1889.

But Rayleigh* is of opinion that there is no such change in the coefficient, while Callendar and Barnes state that any such variation from the normal value is merely temporary in character. There does not appear to be much doubt, however, that the temperature coefficient in such a case is much less definite.

As would be expected, the lag in **H**-form cells is very much less than in the Board of Trade form. This is clearly shown by the curves B, C and D in Fig. 168, which are due to Spiers, Twyman and Waters.† The Authors find that about half the lag in the **H**-form is due to lag of the cell's temperature behind that of the bath.

PORTABLE CLARK CELLS.—The ordinary Clark cell is portable inasmuch as it may be carried from place to place without difficulty; but if it is roughly handled the mercury may come in contact with the zinc and thereby render the cell useless. A standard cell is said to be portable when it may be inverted without injury.

Portability may be gained in various ways. The most usual method is to eliminate the mercury by using an amalgamated platinum wire or plate; but complete amalgamation is not easily effected. Probably the simplest way of amalgamation is to dip heated platinum into boiling or nearly boiling mercury, instead of the usual method of dipping the heated platinum into cold mercury. Kahl‡ gives the following instructions for setting up portable **H**-form cells with amalgamated platinum as one of the plates :—

The containing vessel is first filled with aqua regia and heated in a sand bath until a rapid development of gas takes place at the platinum. Then rinse with water, pour mercury into the branch intended to contain the zinc amalgam, and fill the entire vessel with a concentrated solution of

* *The Electrician*, Vol. XXIV., p. 285, 1889.

† *Phil. Mag.*, Series V., Vol. XLV., p. 285, 1898.

‡ *The Electrician*, Vol. XXXI., p. 265, 1893.

mercurous nitrate containing a little nitric acid. Then connect the mercury with the positive and the platinum foil with the negative pole of a battery, and send a current of about 0.5 ampere through the solution until the platinum foil is covered over with firmly-attached mercury globules. The whole process lasts about five minutes. Finally the vessel is thoroughly rinsed with distilled water until not a trace of the nitrate remains.

The zinc amalgam is introduced with the precautions previously mentioned. After cooling, it is covered with zinc sulphate crystals, to which some concentrated zinc sulphate solution is added, so as to just cover them. The vessel is allowed to stand for two days, so that the crystals may settle closely and form a layer impenetrable to the paste, with which the whole vessel is finally filled up.

Carhart has suggested the insertion of a diaphragm of cork between the zinc and mercury in the Board of Trade form of cell. A porous pot was used for the same purpose by Feussner,* but this causes the cell to follow temperature variations more slowly, and appears to increase the E.M.F. to $\frac{3}{100}$ of a volt above that of the H-form.

In Carhart's portable cell† the zinc is cast with a foot which nearly fills the tube and is turned down so as to form a flat plate. This rests upon a wad of purified asbestos, which separates the mercurous sulphate paste from the saturated zinc sulphate solution, and thus secures portability. Crystals are placed above the zinc plate (but are not shown in Fig. 169), and also in the paste as usual.

The zinc stem is protected by a glass tube cemented to it with an insulating wax, and thus it is in contact with the zinc sulphate solution only where the crystals are in excess. Before sealing, the cell is closed with a thin slip of cork, previously boiled in paraffin. Connection with the mercury is effected by a platinum wire sealed into the glass.

In the well-known portable cells of **MUIRHEAD**, the mercury of the Board of Trade cell is replaced by a flattened spiral of fine platinum wire containing a small quantity of

* *Zeitschrift für Instrumentenkunde*, Vol. VIII., p. 300, 1893.

† *The Electrician*, Vol. XXXV., p. 844, 1895.

mercury. This spiral is shown enlarged on the right of Fig. 170. In setting up the cell, the platinum spiral is heated to redness and plunged into mercury, which is retained to some extent by the spiral. Contrary to the method used in setting up the Board of Trade cell, the cork, with the zinc and platinum in place, is first pushed into its final position in the tube, the ingredients being introduced through the hole A, which is afterwards closed by a small piece of cork.

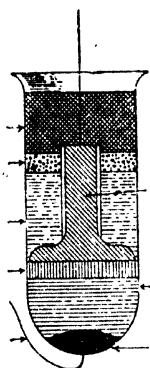


FIG. 169.—Carhart's Portable Clark Cell.

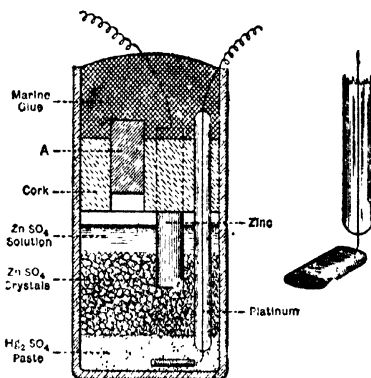


FIG. 170.—Muirhead's Portable Clark Cell.

Muirhead's method of preparing the paste is of interest on account of the simplicity of the method as compared with that given in the Board of Trade specification, and also by reason of the excellent results attained, notwithstanding this simplification. The zinc sulphate is prepared by adding the crystals to an equal bulk of water heated to boiling. When the crystals are completely dissolved, the solution, without boiling, is allowed to cool. Crystals begin to form at about 30°C ., and a good yield is obtained if the solution is allowed to stand until the next day. No

precautions are taken to avoid acidity. The mercurous sulphate is washed by decantation and left to dry to some extent, after which it is mixed with a little mercury and a large proportion of the prepared crystals. The mixture is warmed to, say, 50°C ., and shaken until the mixing is thorough and the mercury is distributed throughout the mass. Boiling is avoided, as it gives rise to a hard crystalline formation. It is found advisable to leave the paste at least six months before use; this probably allows any

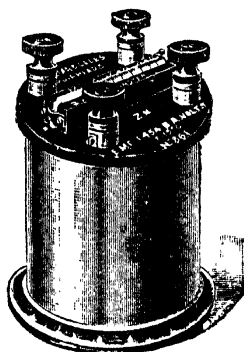


FIG. 171.—Muirhead's Standard Cells.

necessary neutralisation to take place, and gives rise to more constant results.

This simple method, which has been in use for many years, forms the basis of the specification drawn up by Dr. Muirhead for the Electrical Standards Committee, but it was superseded by the more complicated, though apparently less accurate, specification of the Board of Trade. Dr. Muirhead states that the cells agree among themselves to one part in 5,000.

In setting up a cell of this kind the paste is shaken up, being warmed if necessary, and introduced by means of a

small funnel, more of the prepared crystals being added if required. The paste slowly settles to the bottom, covering the platinum spiral, and leaves the zinc free from the paste but surrounded by a large quantity of crystals, which gradually set into a compact mass and remain undisturbed even if the cell is inverted. There is, therefore, no tendency for the mercury to leave the spiral.

Fig. 171 shows the usual form in which Clark cells are mounted for laboratory use. The case contains two cells and a thermometer. A comparison of the cells affords some indication as to whether the standard is changing or is maintaining its value, as it is unlikely that both cells would vary to the same extent. This method of mounting is convenient for general laboratory work, but is unsuitable if high accuracy is required, as the thermometer is short, and therefore can only be read approximately, and, further, the temperature of the thermometer is not necessarily that of the cells.

OTHER FORMS OF CLARK CELLS.—Various other forms of Clark cell have been proposed from time to time, but have little more than historical interest. Thus, Callendar and Barnes* sought to overcome the diffusion lag in the Board of Trade cell by setting it up in an inverted form, using zinc amalgam and platinum wire both in contact with a mass of crystals, so that diffusion lag cannot exist to an appreciable extent.

Callendar and Barnes† have also made what they term "Crystal" cells, in which the clear solution in the ordinary form of cell is replaced by moist zinc sulphate crystals. These cells were also made in an hermetically sealed form by fusing the glass tube.

* *British Association Report*, 1897, p. 591; *The Electrician*, Vol. XXXIX., p. 638, and Vol. XL., p. 165.

† *Proceedings*, Royal Society, Vol. LXII., p. 117, 1897; *Physical Review*, Vol. X., p. 268, 1900.

THE WESTON, OR CADMIUM, CELL.

The chief objection to the Clark cell is its high temperature coefficient, which makes the value of the E.M.F. somewhat uncertain for work of the highest accuracy, unless the temperature of the cell is carefully controlled. Also, if the temperature of the cell is allowed to vary, there is some uncertainty produced by lag, even in the H-type. The temperature coefficient is largely due to the fact that the solubility of zinc sulphate varies a great deal with the temperature; the density of the solution, therefore, changes with the temperature and produces a corresponding change in the E.M.F., and the stable condition is only reached after a certain period, as it depends upon solution or crystallisation, as the case may be, and upon diffusion. In order to reduce the temperature coefficient so as more or less to eliminate temperature corrections, E. Weston* selected cadmium sulphate, in place of zinc sulphate, as being a salt whose solubility changes but slightly with temperature, and a cadmium alloy in place of zinc. In other words, the Weston cell is the same as the Clark cell, except that cadmium takes the place of zinc throughout. In this way the temperature coefficient is reduced to 0.004 per cent., and may often be neglected. It should be noted, however, that the temperature coefficient of either element of a Weston cell is considerable; these individual coefficients are opposed to each other, and largely cancel, so that the temperature coefficient of the cell as a whole is very small, but for this effect to hold it is necessary for both legs of an H-form cell to be at the same temperature.

The Weston cell was recommended as a standard by the International Conference on Electrical Units and Standards, which met in London in 1908. It therefore has a certain international standing, but so far it has no legal standing in

* *The Electrician*, Vol. XXX., p. 741, 1893.

the United Kingdom. In a schedule to the report of the Conference the Weston normal cell is described as follows :—

WESTON NORMAL CELL.

The Weston normal cell may be conveniently employed as a standard of electric pressure for the measurement both of E.M.F. and of current, and, when set up in accordance with the following specification, may be taken, provisionally,* as having, at a temperature of 20°C., an E.M.F. of 1.0184 volts.†

The Weston normal cell is a voltaic cell which has a saturated aqueous solution of cadmium sulphate ($\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$) as its electrolyte.

The electrolyte must be neutral to congo red.

The positive electrode of the cell is mercury.

The negative electrode of the cell is cadmium amalgam consisting of 12.5 parts by weight of cadmium in 100 parts of amalgam.

The depolariser, which is placed in contact with the positive electrode, is a paste made by mixing mercurous sulphate with powdered crystals of cadmium sulphate and a saturated aqueous solution of cadmium sulphate.

The different methods of preparing the mercurous sulphate paste are described in the notes.‡ One of the methods there specified must be carried out.

For setting up the cell, the H-form is the most suitable. The leads passing through the glass to the electrodes must be of platinum wire, which must not be allowed to come into contact with the electrolyte. The amalgam is placed in one limb, the mercury in the other.

The depolariser is placed above the mercury and a layer of cadmium sulphate crystals is introduced into each limb. The entire cell is filled with a saturated solution of cadmium sulphate and then hermetically sealed.

The following formula is recommended for the E.M.F. of the cell in terms of the temperature between the limits 0°C. and 40°C. :—

$$E_t = E_{20} - 0.0000406(t - 20) - 0.0000095(t - 20)^2 + 0.0000001(t - 20)^3.$$

The principal national laboratories, besides the National Physical Laboratory, are the Bureau of Standards at Washington, the Laboratoire Central at Paris, and the Physikalisch-Technische Reichsanstalt at Berlin. The International Conference of 1908 appointed a Scientific Com-

* The specification is subject to modification by the Scientific Committee mentioned below.

† See modification given below.

‡ The intention is that directions should be issued by the Scientific Committee or the Permanent Commission as may be found necessary.

mittee to carry out work in connection with standards, and the necessary experimental work is carried out by the above laboratories in collaboration.

The first and most important undertaking for this Committee was to ascertain more definitely the value which should be assigned to the Weston cell. This involved completion of the specifications and a series of experiments with the silver voltameter, whereby the E.M.F. of the cell would be determined from the amount of silver deposited, the resistance and the time. In 1910, delegates from the National Physical Laboratory, the Physikalisch Technische Reichsanstalt and the Laboratoire Central d'Electricité met at the Bureau of Standards at Washington and made numerous experiments with the silver voltameter and Weston cells. Each delegate from Europe took a number of cells (84 in all), and these were compared with a fourth lot at Washington. The mean E.M.F. of all the cells agreed with the mean E.M.F. of each group within less than 0.00001 volt.

New Weston cells were also set up at Washington with materials from Teddington, Paris, Berlin and Washington. The mercurous sulphate was made by the delegates at the Bureau of Standards. Comparison of the various cells showed agreement within from 2 to 3 parts in 100,000. As a result of such work and other work on the silver voltameter, it was announced in 1911 by the National Physical Laboratory that the E.M.F. of the Weston cell had been determined to be 1.0183 international volts at 20°C. (as against the provisional value of 1.0184 volts recommended by the Conference), and that this value would thenceforth be used by the National Physical Laboratory. Similar statements were issued by the Bureau of Standards and by the Reichsanstalt.*

* *The Electrician*, Vol. LXVI., p. 742, and *Nature*, Vol. LXXXV., p. 508, 1911.

The above is only a brief official description. There is so far no international agreement as to the precise methods to be followed in constructing the cell, and therefore some notes on various methods and investigations may prove of value.

METHODS USED AT THE NATIONAL PHYSICAL LABORATORY (1907).—The method adopted at the National Physical Laboratory was last described in 1907,* and is as follows :—

PREPARATION OF THE WESTON (CADMIUM) STANDARD CELL (PROVISIONAL DIRECTIONS BY THE NATIONAL PHYSICAL LABORATORY).

Definition of the Cell.—The cell has mercury for its positive electrode and an amalgam of cadmium, consisting of $12\frac{1}{2}$ parts by weight of cadmium to $87\frac{1}{2}$ parts of mercury, for its negative electrode. The electrolyte consists of a saturated solution of cadmium sulphate, and solid cadmium sulphate is contained within the cell. A paste consisting of solid mercurous sulphate, mercury and cadmium sulphate rests on the positive electrode.

PREPARATION OF THE MATERIALS.

1. *Mercury.*—Commercially pure mercury should be squeezed through washleather and passed in the finely divided condition in which it emerges through dilute nitric acid (1 part of acid to 6 parts of water) and mercurous nitrate solution, and afterwards through distilled water. These liquids are conveniently contained in long glass tubes. The mercury is then distilled twice in vacuo. Mercury suspected of any abnormal contamination should not be employed.

2. *Cadmium Amalgam.*—A current is passed from a thick rod of pure commercial cadmium to distilled mercury, the intervening liquid being cadmium sulphate solution rendered slightly acid with a few drops of sulphuric acid. The cathode is weighed before electrolysis commences, and again afterwards; the percentage of cadmium in the amalgam is then calculated. More than the requisite amount of cadmium should be deposited, and the percentage reduced to $12\frac{1}{2}$ by the addition of mercury. To prevent the anode slime having access to the cathode the anode should be contained in a filter-paper cup, as in the Rayleigh form of silver voltameter. Contact with the cathode is made by a platinum wire sealed into a glass tube, the wire being thus protected

* Report of the Electrical Standards Committee of the British Association.

from direct contact with the cadmium sulphate solution. An approximate estimate of the quantity of cadmium deposited is obtained from the readings of an ammeter placed in the circuit. The amalgam, with very dilute sulphuric acid flooding its surface, is melted over a water bath and stirred to ensure homogeneity. It is then ready for use.

3. *Cadmium Sulphate*.—Procure commercially pure cadmium sulphate, $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$. Powder in a mortar and dissolve in distilled water until a saturated solution results; filter the solution through a fine-grained filter paper until it is quite clear. The liquid should then be placed in a large crystallising dish and slowly evaporated at a temperature of about 35°C ., when, provided that dust is excluded, many transparent crystals of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ will result. In this way about five-sixths of the solution may be evaporated (the mother liquid may be used for a preliminary washing of the mercurous sulphate, the manufacture of which is described hereafter). The re-crystallised cadmium sulphate should be washed with successive small quantities of distilled water, until after standing for ten minutes no trace of acidity can be detected in it with sensitive congo-red paper; the crystals, still moist, are transferred to a stock bottle. To prepare the saturated solution the crystals are crushed in a mortar and agitated with distilled water. The latter may be warmed to 35°C .

4. *Mercurous Sulphate*.—Add 15 cubic cm. of pure strong nitric acid to 100 grammes of pure mercury contained in a crystallising dish, and place on one side until the action is over, or nearly over. Transfer the mercurous nitrate thus formed, together with the excess of mercury, to a beaker containing about 200 cubic cm. of dilute nitric acid (1 of acid to 40 of water by volume); a clear solution should result. Prepare about 1 litre of dilute sulphuric acid (1 of acid to 3 of water by volume), and while the mixture is hot add the acid mercurous nitrate solution to it. The solution should be added as a very fine stream from the narrow orifice of a pipette, and the mixture violently agitated during the mixing. Mercurous sulphate is precipitated and rapidly settles to the bottom of the vessel, when the stirring ceases. Decant the hot clear liquid and wash the precipitate twice by decantation with dilute sulphuric acid (1 of acid to 6 of water by volume). The precipitate should then be filtered. (A small Buchener filter funnel and a filter flask is very convenient for this latter operation.) Wash the precipitate three times with the dilute sulphuric acid (1 to 6), and afterwards wash six or seven times with saturated cadmium sulphate solution to remove the acid. After each washing the liquid should be removed as completely as possible by the filter pump. When these operations are complete the mercurous sulphate is flooded with saturated cadmium sulphate solution and left for one hour; the solution is then tested with congo-red paper. In general no acid will be detected, and the mercurous sulphate is ready for use. It is placed in a stock bottle, together with some saturated cadmium sulphate solution, and should be kept in the dark. If acid is detected, the washing

must be continued. When the cells are required for observations of the highest precision, the apparently neutral mercurous sulphate should not be immediately used. It is placed in a bottle with saturated cadmium sulphate solution, and at the end of one week the latter is tested for acidity. The sulphate is given another washing with the solution, and may then be used if only a trace of acid is detected.

One of the following methods of preparation may, if desired, be substituted for the foregoing :—

1. *Electrolytic Method.*—This preparation is conducted in a darkened room. Pure distilled mercury forms the anode and platinum foil the cathode, the electrolyte being dilute sulphuric acid (1 volume of acid to 5 volumes of water). The mercury is placed in the bottom of a large flat-based beaker, and about twenty times its volume of the dilute acid is added. Contact with the mercury is made by a platinum wire passing through a glass tube, and the cathode is suspended in the upper portion of the liquid. During electrolysis the electrolyte must be continually stirred, an L-shaped glass stirrer being very efficient, the foot of the L moving close to the surface of the mercury. A convenient current density is 0.01 ampere per square centimetre of anode surface. The mercurous sulphate so prepared is filtered, and the greater part of the mercury removed; it is then washed with dilute sulphuric acid and saturated cadmium sulphate solution in a manner already described for the previous preparation.

2. *By Means of Fuming Sulphuric Acid.*—Place distilled mercury in a crystallising dish so as just to cover the bottom. Add sufficient fuming sulphuric acid to flood the surface of the mercury to a depth of 2 mm. Cover with a clock glass and place on one side for 48 hours. Mercurous sulphate is formed and appears in the crystalline form. Carefully add the salt to hot dilute sulphuric acid (1 to 6) and well agitate. Decant the hot liquid. If any caked masses of the sulphate are left these should be rejected or crushed in an agate mortar. Wash three times by decantation with hot dilute sulphuric acid, and afterwards filter and wash with saturated cadmium sulphate solution in the manner already described. Set aside with cadmium sulphate solution for one week at least, test for acidity, and wash as described for the first preparation.

The Mercurous Sulphate Paste.—The mercurous sulphate is mixed with about one-fourth its volume of powdered re-crystallised cadmium sulphate, and about one-tenth its volume of pure mercury. (When the electrolytic sulphate is used, or that prepared with fuming sulphuric acid, no mercury need be added.) To the mixture of mercurous sulphate, cadmium sulphate and mercury, sufficient saturated cadmium sulphate solution is added, so that when well mixed the whole forms a thin paste.

Setting Up the Cell.—That type of H-form of cell which may be hermetically sealed is the most convenient; if the lower end of each limb

is slightly constricted, the contents of the cells are less liable to be disturbed. The platinum wires inside the glass vessel are amalgamated by passing an electric current from a platinum wire anode through an acid solution of mercurous nitrate to each of the wires in turn as a kathode. The vessel is washed out twice with dilute nitric acid, several times with water, and finally with distilled water; it is dried in an oven. A small pipette is used for the introduction of the amalgam, and a small thistle funnel for the insertion of the paste and crystals. The main stock of amalgam is flooded with very dilute sulphuric acid, and it is melted over a water bath; a little of it is introduced into one of the limbs of the H-vessel. After the amalgam has solidified this limb must be washed out several times with distilled water, care being taken to avoid wetting the interior of the other limb. A little distilled water is added, and the amalgam is melted by immersing the limbs of the H-vessel in hot water. After the solidification of the amalgam it is washed once more with distilled water. Into the other limb sufficient mercury is introduced to cover the amalgamated platinum wire; then the paste is added, care being taken not to smear the sides of the vessel. Finally, powdered crystals of cadmium sulphate are introduced into each limb, and saturated cadmium sulphate solution is added. The cell may be immediately sealed with the aid of a blowpipe, but the contents must not be abnormally heated thereby. The cadmium amalgam introduced should cover the amalgamated platinum wire. The depth of the paste should be from 0.5 cm. to 1.0 cm., and the depth of the layer of crystals about 0.5 cm. Twenty-four hours after the cell has been set up it may be used. Its E.M.F. at 15°C. is 1.108₅ volts.

Temperature Coefficient.—The E.M.F. at any other temperature may be obtained from the formula given by the Phys. Techn. Reichsanstalt—viz.,

$$E_t = E_{10} - 0.000038(t - 20) - 0.00000065(t - 20)^2,$$

or from the formula obtained at the National Physical Laboratory,

$$E_t = E_{17} - 0.000034_6(t - 17) - 0.00000066(t - 17)^2.$$

This specification is based on observations made at the National Physical Laboratory.

In a later brief statement by the British Association Committee,* it is mentioned that the amalgam may be made either by electro-deposition or by mechanical mixing. It should be fused and freed from oxide by washing with dilute sulphuric acid.

When the cadmium sulphate is very impure the procedure recommended by the National Physical Laboratory is very

* Report of the Electrical Standards Committee of the British Association, 1908.

similar to that employed for the purification of zinc sulphate. An excess of cadmium oxide and a little hydrogen peroxide are added, and the solution heated on a water bath for four hours. It is then filtered, and crystals are separated from it at a comparatively high temperature. These crystals are washed, dissolved in water made slightly acid (to the extent of 2 parts in 10,000) with sulphuric acid, and the crystallising processes already described are carried out.

METHODS USED AT THE BUREAU OF STANDARDS.

Very detailed directions have also been published by F. A. Wolff and C. E. Waters, of the Bureau of Standards.* These directions are largely similar to the instructions given above, but there are certain differences. For the preliminary purification of mercury, electrolysis is mentioned as an alternative method, using a platinum cathode in 2 per cent. nitric acid and a current density of 0.1 ampere per square dm. The more electro-positive impurities thus pass into solution. For secondary standards, pure commercial zinc and cadmium may be used; otherwise, the pure metal is made by electrolysis, say from a solution of the sulphate or by distillation. The cadmium sulphate is purified by re-crystallisation. In the case of zinc sulphate, electrolysis may be employed with platinum electrodes, and a current density of 0.1 ampere per square dm.; this is continued until a clean anode no longer shows the formation of a film of lead peroxide, thus demonstrating the absence of lead. For making amalgams, the zinc or cadmium, as the case may be, is first treated with dilute sulphuric acid to remove oxide, and is then washed; the required quantity is then treated with the mercury. It is

* "Preliminary Specification for Clark and Weston Standard Cells," *Bulletin of the Bureau of Standards*, Vol. III., p. 623, 1907; and Vol. IV., p. 1, 1907. The latter is mostly given in *The Electrician*, Vol. LX., pp. 674 and 711, 1908.

preferable, however, to use the electrolytic method. The tarnishing of amalgams is not important. Commercial mercurous sulphate may contain basic mercurous sulphate, basic mercuric sulphate, traces of nitrate and other impurities. Pure mercurous sulphate hydrolyses in water, and even in dilute sulphuric acid, so that washing with water, as previously specified, should not be adopted. Commercial mercurous sulphate gives an E.M.F. higher than the normal, but this gradually falls. The size of grain may have an effect on the E.M.F., and it should be remembered that mercurous sulphate is acted upon by light. Pure mercurous sulphate may be prepared (1) by electrolysis, the mercury and acid being stirred to prevent the formation of mercuric sulphate; (2) by forming nitrate from mercury, and thence the sulphate; (3) by combining the steps and acting upon mercury by sulphuric acid (1 part of acid to 2 of water), containing a small percentage of nitric acid; (4) by the reduction of mercuric sulphate with mercury; (5) by recrystallising commercial mercurous sulphate. For secondary standards commercial mercurous sulphate may be digested with hot dilute sulphuric acid and mercury for three hours at a temperature of 100°C . with vigorous stirring.* In making up the paste, if the mercurous sulphate is kept in acid, the salt must be washed first with sulphuric acid to remove any mercuric sulphate and then with alcohol. If the mercurous sulphate is white, mercury should be added in making the paste.

ELECTROLYTIC METHODS OF PREPARING MERCUROUS SULPHATE.—Undoubtedly the most sensitive constituent of standard cells is the mercurous sulphate, and much labour has been spent in its investigation. The

* A similar method is recommended by C. J. J. Fox (*The Electrician*, Vol. LXIII., p. 835, 1909), the temperature being 120°deg . to 150°deg ., and the time of heating extending to a day or so.

various methods have been discussed by F. E. Smith.* The preparation of this salt has also been investigated by G. A. Hulett,† who prefers the electrolytic method. In using this method, as already mentioned, care must be taken to keep the newly formed mercurous sulphate from lying on the surface of the mercury. On this account it is an advantage to use an inner vessel for the mercury, as shown in Fig. 172, so that a good deal of the sulphate in suspension finds its

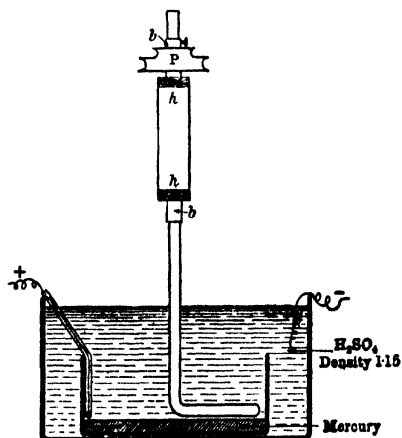


FIG. 172.—Arrangement for Electrolytic Production of Mercurous Sulphate (Hulett).

way into the outer vessel, where it can settle to the bottom without doing any harm. The stirrer is made of glass rod, as shown, the horizontal arm being just above the surface of the mercury. The vertical part is held by a brass tube, *b*, which runs in bronze bearings in the tube *h*. A pulley, *P*,

* Report of the Electrical Standards Committee of the British Association, 1904.

† *Physical Review*, Vol. XXXII., p. 257; *The Electrician*, Vol. LXVII., p. 129, 1911.

is provided, and the stirrer is driven at about 200 revs. per min. With fresh acid a skin forms on the surface of the mercury; but after interrupting the current several times, until the acid becomes saturated and the solid sulphate appears in suspension throughout the acid, there is no further trouble. The current density employed is from 1 to 2 amperes per square dm. of mercury anode sur-

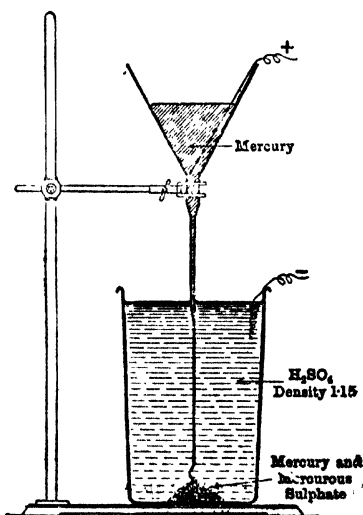


FIG. 173.—Electrolytic Production of Mercurous Sulphate with a Mercury Jet (Hulett).

face. The resulting sulphate is grey, from the presence of finely divided mercury, which is an advantage, as it checks any tendency to oxidation. Usually 50 or 60 grammes of the sulphate were prepared in one run.

A simpler method is illustrated in Fig. 173. The difficulty of stirring is here eliminated by using the mercury as the anode and running it into the bath in a fine stream.

For this purpose the stem of the funnel is drawn out into a capillary of such a bore that it takes about five minutes for 10 c.c of mercury to run through. The tip is allowed to dip below the surface of the acid, of which the specific gravity is 1.15. The mercury forms a spray on entering the acid until the current (of 2-3 amperes) is allowed to flow, when the drops coalesce into a thread, which is mostly grey in colour, from the formation of sulphate.

Alternating current has also been used for preparing mercurous sulphate, and this procedure is favoured by the Laboratoire Central d'Electricité at Paris. This method can be easily used by employing two streams of mercury flowing into the same beaker of acid, the mercury in the two funnels being used as the two electrodes. Hulett used a current of 5 amperes at a frequency of 60; the efficiency was as high as with continuous current, and the resulting salt seemed to be the preferable of the two. The sulphate prepared by flowing electrodes is white.

The sulphuric acid is generally removed from the mercurous sulphate by washing with alcohol; but Hulett states that three washings with saturated cadmium sulphate are sufficient with proper precautions, the alcohol being omitted.

SIZE OF GRAIN OF THE MERCUREOUS SULPHATE.—

It is generally recognised that the mercurous sulphate crystals should not be so small as to have an abnormal solubility, or so large as to be inefficient as a depolariser.

The size of grain is a curious point which has been investigated by H. v. Steinwehr.* Very large crystals of mercurous sulphate were prepared, and these were used partly in this form and partly as fine crystals obtained by pounding the large crystals. A difference in E.M.F. amounting to 0.0006 volt was found between the fine and the large crystals, the fine crystals giving the higher E.M.F. It is difficult to

* *Zeitschrift für Instrumentenkunde*, Vol. XXV., p. 205, 1905.

understand this result, except in so far as fine grains have a greater solubility, and therefore would give a higher E.M.F., but such an increase would probably be so small as to be negligible. G. A. Hulett,* on experimental evidence, denies the results obtained by H. v. Steinwehr, and attributes them to hydrolysis. F. E. Smith† also failed to confirm v. Steinwehr's results.

THE FORM OF CELL.—The following directions are given by the British Association.‡ The H-form of cell due to Lord Rayleigh is the most convenient, and is in general use. Two patterns have been adopted. In Fig. 174 a form is shown in which the electrodes are sealed into the lower ends of the two vertical limbs, while in the form shown in Fig. 175 the electrodes pass through the glass tubes into the lower ends of which they are sealed. Form 1 can be hermetically sealed, and is intended to be immersed in an insulating liquid. Form 2 is sealed with marine glue, and may be immersed in ice or water. The hermetical sealing of form 1 was suggested by Lord Rayleigh§ and later by Prof. Carhart.|| The glass tubes through which the electrodes are introduced in form 2 pass through corks which have been previously boiled in water and soaked in cadmium sulphate solution. In addition to the hole which allows of the passage of the electrode, a second hole is bored through these corks for the passage of small glass pipettes. After the cell is filled, these additional holes are fitted with small corks, and the cell is finally sealed with marine glue. The position of the various parts is shown in the figure

* *Physical Review*, Vol. XXII., p. 321, 1906; *The Electrician*, Vol. LVII., p. 708, 1906.

† *Phil. Trans. (A)*, Royal Society, Vol. CCVII., p. 393, 1906.

‡ Appendix to Report of the Electrical Standards Committee of the British Association, 1905.

§ *Phil. Trans.*, Vol. CLXXVI., p. 42, 1886.

|| St. Louis Congress, 1904.

(Both forms of glass vessels are stocked by A. C. Cossor, Ltd., of 59-61, Clerkenwell-road, London, E.C.)

It is sometimes found that the cell cracks where the platinum which makes contact with the amalgam is sealed into the glass. Such cracking practically never occurs with Weston cells. The difficulty with Clark cells may be

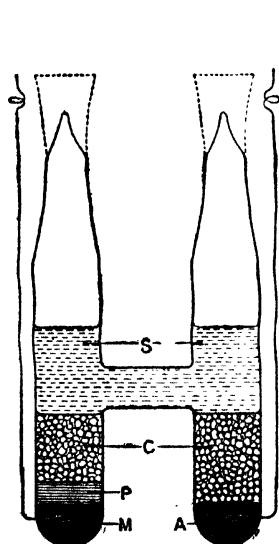


FIG. 174.

A=Amalgam.
C=Cadmium sulphate crystals.
G=Marine glue.
K=Cork.

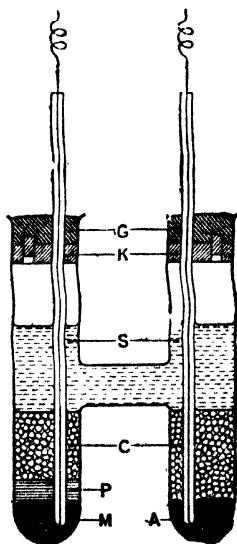


FIG. 175.

M=Mercury
P=Paste.
S=Saturated solution of cadmium sulphate.

avoided by sealing glass capillaries over part of the platinum wires inside the cell. When these capillaries are about 5mm. long the cells last for a great many years. At the National Physical Laboratory cells of this kind constructed eight years ago are still in good condition. With Kahle's form,

shown in Fig. 176, there is no trouble. In this form a side tube is used, and the platinum is carried down about 2 cm. below the seal. While the amalgam is still liquid it is sucked half-way up the platinum and allowed to solidify. In this form of construction there is also less chance of the platinum making contact with the electrolyte. The other terminal should be covered with mercury to a depth of at least 10 mm. In sealing off the cell, a cork which fits the

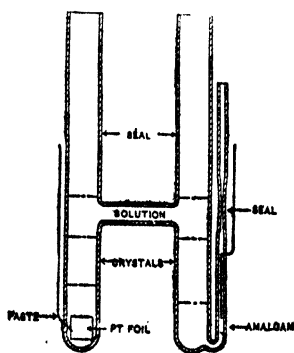


FIG. 176.—Kahle's form of Cell.

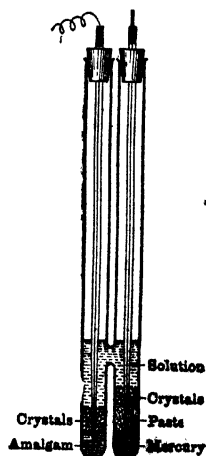


FIG. 177.—Hulett's Cell.

tube and has a glass rod extending from it may be conveniently used for drawing out the heated tube.

G. A. Hulett* advocates the type shown in Fig. 177, with very much longer vertical limbs (20 cm. long). The cross tube is at the same height as in the shorter form, and the solution is only carried up a little above the cross

* *Physica Review*, Vol. XXXII, p. 257, 1911; *The Electrician*, Vol. LXVII, p. 129, 1911.

tube. There is, therefore, a long free space above the solution. The electrode wires may be made up of copper, with platinum at the end for sealing and to act as electrodes in the cell. This longer form has the advantage that cells can be conveniently bound together and can be placed in a deep bath, so that the temperature conditions are good and yet the insulation is not impaired. Tube electrodes, as compared with those which are sealed into the cell, have the advantage that they can be amalgamated by holding them for a few minutes in boiling mercury in a test tube.

PORTABILITY.—At the National Physical Laboratory, in order to make standard cells portable, constrictions are made in the lower ends of the tubes and a thick layer of finely pounded cadmium sulphate crystals is introduced into each limb above the paste and the amalgam respectively. Saturated cadmium sulphate is then added, and the cells are exposed in a warm room for a week or more to allow some of the liquid to evaporate, and thus to cement together the loose crystals. This crystalline plug keeps the contents in their proper place, and enables the cell to be sent by post without risk of the constituents being displaced.

The only objection to this method is that the internal resistance is high and varies from cell to cell, and in hot climates the plug must be very thick to allow for crystals passing into solution at the higher temperatures. On the other hand, care must be taken, if some other material is used as a plug, not to introduce harmful bodies. This difficulty has been overcome by H. Tinsley,* who, as a manufacturer, can speak with authority on the subject, by using a cork ring on the under side of which is sewn a linen disc, thus forming a small drum head. This is forced down on to the top of the cadmium sulphate crystals. The

* *The Electrician*, Vol. LXV., p. 568, 1910.

linen is freed from its dressing by prolonged boiling in water. For hot climates a few crystals are added above the drum head to maintain saturation. This form of construction, which is shown in Fig. 178, is stated to be very satisfactory. The internal resistance in this type of cell is 700-800 ohms, whereas in the older type the figure varies from 1,000 to 2,600 ohms, judging by Tinsley's tests of five cells.

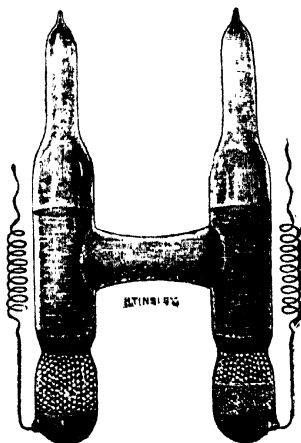


FIG. 178.—Tinsley's Portable Form of Cell.

In order to secure portability, a special form of cell has been proposed by R. E. de Lury.* A single straight tube is used divided into two compartments about half-way along its length by means of a plug of asbestos. The mid part of the tube in both directions is shaped on the principle of an unspillable ink bottle, so that any free mercury cannot pass from one end to the other.

* *Physical Review*, Vol. XXV., p. 492, 1907; *The Electrician*, Vol. LX., p. 805, 1908.

E.M.F. OF H AND BOARD OF TRADE TYPES.—

In 1892 it was stated by Kahle, in a Paper read before the British Association, that the H-form of cell had an E.M.F. 0.0004 volt lower than the tube form adopted by the Board of Trade. This statement was generally accepted, but later work by F. E. Smith* has shown that there is no foundation for this view, for either Clark or Weston cells.

EFFECT OF COMPOSITION OF THE AMALGAM.—

There has been considerable discussion on the percentage of cadmium that should be used in the amalgam. Many observers have noticed variations of E.M.F. which they have attributed to the amalgam, but the observations have not infrequently been at variance.

A careful study of the subject has been made by F. E. Smith,† who found that the E.M.F. properties of an amalgam depend upon whether it is wholly solid, partly solid and partly liquid or wholly liquid—that is, upon whether there are present one or two phases, as it is termed. If a body is partly liquid and partly solid, there are two phases present, the liquid and the solid. If a solid amalgam is heated, at the moment of transition from the single phase to two phases there is an immediate change in the temperature coefficient of the E.M.F. between the amalgam and a solution of cadmium sulphate, and there is again a change when the amalgam becomes wholly liquid. When there are two phases and the temperature is varied the relative proportions of the phases change, but the E.M.F. does not vary; and thus stable amalgams containing different percentages of cadmium, but possessing the two phases, have the same E.M.F. towards a solution of cadmium sulphate. On the other hand, if the amalgam is

* Report of the Electrical Standards Committee of the British Association, 1904.

† *Proceedings*, Physical Society of London, Vol. XXII., p. 11; *Phil. Mag.*, February, 1910, p. 250.

wholly liquid or wholly solid, the E.M.F. varies with the percentage of cadmium. This is seen from Fig. 179, which shows the variation of E.M.F. with percentage of cadmium for various temperatures.

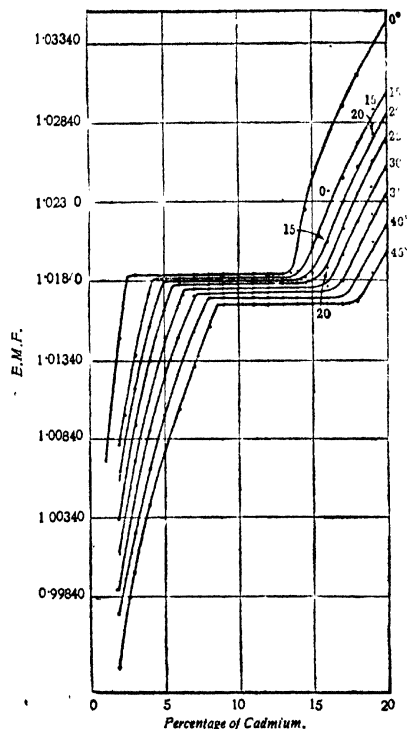


FIG. 179.—Curves showing the variation of the E.M.F. with the percentage of Cadmium in the Amalgam (F. E. Smith).

It follows, therefore, that instability will occur at both transition points when the amalgam becomes wholly liquid or wholly solid. Although melting points and freezing

points are definite, the completion of the change to all liquid or all solid may take a considerable time if the temperature of the cell is near the transition point and during this time the E.M.F. must vary. Moreover, the condition of the amalgam varies with the heat treatment that it has experienced.

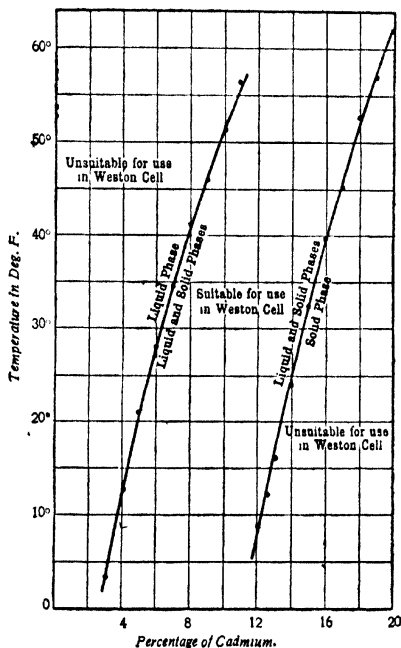


FIG. 180.—Diagram showing the Limits of Temperature for Different Amalgams (F. E. Smith).

For example, slow cooling would tend to give an upper layer richer in cadmium than lower down, whereas rapid cooling would give a more uniform composition.

Thus the conclusion is reached that the percentage of cadmium should be such that the two transition points are

outside the range of ordinary working temperatures. This is indicated in Fig. 189. From this diagram it is seen that a $12\frac{1}{2}$ per cent. amalgam has a transition point to the solid state that is undesirably high ($12.1^{\circ}\text{C}.$), and, consequently, F. E. Smith recommends a 10 per cent. amalgam rather than the $12\frac{1}{2}$ per cent. amalgam which has so far been adopted for the normal cell. Fortunately, at temperatures down to $0^{\circ}\text{C}.$, a $12\frac{1}{2}$ per cent. amalgam may still be in a two-phase condition, owing to differences in concentration, and thus the E.M.F. is not necessarily affected.

The working temperatures in Table X. are given by F. E. Smith* for amalgams containing from 6 per cent. to 15 per cent. of mercury:—

Table X.—*Temperature Limits for Various Amalgams.*

Percentage of cadmium in the amalgam.	Limits of temperature for use of Weston cell.	
	Lower limit.	Upper limit.
6	Below $0^{\circ}\text{C}.$	$27.7^{\circ}\text{C}.$
7	"	34.6°
8	"	41.0°
9	"	46.0°
10	"	51.0°
11	About $0^{\circ}\text{C}.$	56.0°
12	8.7°	60.0°
12.5	12.1°	above 60°
13	16.1°	"
14	24.0°	"
15	32.5°	"

The results of this investigation are explained in a Paper by S. W. J. Smith† in terms of the theory of alloys and solutions. It follows from the process of crystallisation that the surface of a slowly cooled amalgam will generally contain a lower percentage of cadmium than the material as a whole, and may even be fluid, although, according to the temperature and composition, the amalgam should be a

* *Loc. cit.*

† *Proceedings, Physical Society of London*, Vol. XXII., p. 369
Phil. Mag., July, 1910, p. 206.

uniform solid. Thus, the E.M.F. with a quickly cooled amalgam may be higher than with one of the same composition cooled slowly, as was, indeed, found by F. E. Smith.

TEMPERATURE COEFFICIENT AND LAG.—The temperature coefficient is approximately -0.00004 volt per degree in the neighbourhood of 20°C ., so that temperature variations are often negligible.

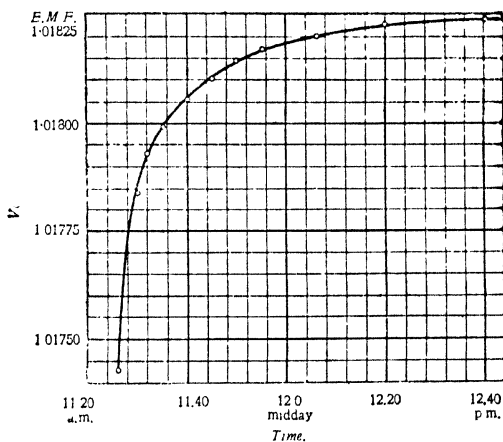


FIG. 181.—Recovery Curve of Cell suddenly cooled from 55°C . to 17°C . (F. E. Smith.)

The lag of E.M.F. with respect to change in temperature is also very much less than in the case of the Clark cell, the actual extent of the lag depending, however, upon the construction of the cell. Fig. 181 is given by F. E. Smith* to illustrate an extreme case. It refers to a cell of the usual H-form which was initially at a temperature of 55°C . (for the preceding 12 hours), and was then immersed in oil at

* *Phil. Trans. (A)*, Royal Society, Vol. CCVII., p. 393, 1908.

17°C. After 20 minutes the E.M.F. was normal to 1 part in 4,000; after a total interval of 40 minutes it was correct to 1 part in 10,000, and after one hour to about 7 parts in 100,000. But it required 14 days to bring the E.M.F. to within 2 parts in 100,000 of the correct value.

HYSTERESIS.—It is sometimes found that, although the E.M.F. of a cell changes with ascending temperature in accordance with the temperature E.M.F. formula, with descending temperatures the E.M.F. changes too rapidly, corresponding to values at temperatures lower than the temperature of the cell by from 3°C. to 15°C. This behaviour is known as “hysteresis,” and is not the same thing as the lagging of E.M.F. behind temperature as described in connection with the Clark cell.

During the last few years this subject has been investigated in detail at the National Physical Laboratory.* It appears that the defect is due partly to hydrolysis† of the mercurous sulphate and partly to complex ions. There is some evidence that complex ions exist both in solutions of cadmium sulphate and in those of mercurous sulphate and cadmium sulphate mixed. In the latter case a molecule of Hg_2SO_4 appears to attach itself to an SO_4 ion. The use of free sulphuric acid was investigated with a view to stopping hydrolysis. It is interesting to note that when the solution in the positive limb is made up with a normal solution of sulphuric acid instead of water the E.M.F. is diminished by 0.01030 volt; when the solution in the negative limb alone is similarly made up with acid the E.M.F. is increased by 0.00965 volt; and when the whole of the

* *The Electrician*, Vol. LXXI., p. 294, 1913; Vol. LXXIII., p. 574, 1914; and Vol. LXXV., p. 463.

† H. S. Carhart and G. A. Hulett (*Transactions, American Electrochemical Society*, Vol. VI., p. 109) express the change by hydrolysis as follows:—



solution in a cell is made up with normal acid saturated with cadmium sulphate, instead of a purely aqueous solution, the E.M.F. is diminished by 0.00065 volt.

The net result, so far, is that a cell will decrease in E.M.F. if the depolariser is partly hydrolysed, the rate of change depending on the extent of the hydrolysis in the layer of salt next to the mercury surface. The formation of complex ions leads to an increase of E.M.F., but the mercury ion concentration diminishes somewhat rapidly in the presence of a large surface of mercury. In any case, a cell should be rejected if it shows hysteresis, because the E.M.F. is not likely to remain constant. It appears that the most constant form of cell is one containing a small quantity of free acid with a grey depolariser, the grey colour being due to the presence of minute globules of mercury.

• **REPRODUCIBILITY.**—The remarkable accuracy with which the Weston cell can be set up is shown by the international experiments* embodied in Table XI. The differences are given between the E.M.F.s of the cells and the reference standards of the various laboratories.

It is interesting to note in an earlier report that of 67 cells (presumably by outside makers) tested in 1909 at the National Physical Laboratory 60 agreed with the Laboratory standards within 1 part in 10,000.

The high degree of reproducibility which has been attained in the making of standard cells is illustrated by 15 Clark cells and 13 Weston cells set up by H. L. Bronson and A. N. Shaw,† according to the specification of Wolff and Waters. These were indirectly compared with the reference cells at the Bureau of Standards, and directly with five cells made at the National Physical Laboratory. The mean of

* Report of the Electrical Standards Committee of the British Association, 1912.

† *The Electrician*, Vol. LXIII., p. 844, 1909; also Vol. LXVI, p. 663, 1911.

Table XI.—*Results of International Comparisons.*

Differences in Microvolts.

B.S.=Bureau of Standards (Washington); N.P.L.=National Physical Laboratory (London); P.T.R.=Physikalisch-Technische Reichsanstalt (Berlin); L.C.E.=Laboratoire Central d'Electricité (Paris).

Standard cell No.	B.S., June & July, 1911.	N.P.L., Aug., 1911.	P.T.R., Sept. & Oct., 1911.	N.P.L., Oct., 1911.	L.C.E., Oct., 1911.	N.P.L., Nov. & Dec., 1911.	B.S., Jan., 1912.
262	— 6	...	— 70	...	— 80	— 60	...
267	41	...	0
268	37	...	— 15
51	— 58	...	— 70	...	— 30
32	— 69	...	— 115	...	— 130
301	— 24	— 5	— 30	...	— 15	...	— 40
304	19	23	0	...	0	...	7
309	— 36	— 27	— 45	...	— 20	...	— 56
310	0	— 4	— 25	...	— 10	...	— 44
A1	— 13	— 12	— 15	...	— 10	...	— 22
43	2	3	— 30	...	5	...	0
44	0	...	— 15	— 7	— 1
19	— 27	...	— 45	— 30	— 28
22	— 31	...	— 40	— 29	— 30
238	— 2	...	20	52	— 10
350	— 24	...	— 20	1	— 24
352	— 31	...	— 45	— 30	— 30
433	30	...	34
142	30	...	33
1-3	— 6	— 5
1-33	— 16	— 16
17	— 5	— 8

the 15 Clark cells was found to differ from the Bureau of Standards Clark cells by less than 14 microvolts. The mean of the 13 Weston cells differed from the Bureau of Standards Weston cells by less than 4 microvolts, and from the mean of Weston cells from the National Physical Laboratory by less than 5 microvolts.

CONSTANTS OF STANDARD CELLS.—In Table XII, are given various determinations of the E.M.F.s and temperature coefficients of Clark and Weston standard cells. The closeness of the values obtained in recent years show the very high accuracy with which the absolute ampere can

now be obtained. It will be noticed that the mean E.M.F. seems lower than the E.M.F. of the Weston cell as officially adopted; but since the results are really expressed in "semi-absolute" volts in absolute determinations this may be explained by the fact that the international ampere is probably a little lower than the absolute ampere.

STANDARD CELLS IN ELECTRICAL MEASUREMENTS.—In using a standard cell it is generally advisable to have a high resistance, say 10,000 ohms, in series with it in order to avoid a short-circuit and consequent polarisation. Usually there is no reason to fear that the small currents required in such tests as are carried out with a potentiometer or a condenser will cause any appreciable polarisation. So far back as 1884, Rayleigh* observed that Clark cells recovered rapidly from the effects of being placed on a circuit of 500 ohms. Callendar and Barnes† are of opinion that short-circuiting is beneficial to new cells which have not yet reached a steady condition, and the present Author has found that Clark cells maintain their condition better when in use than when out of use.

Even a brief short-circuit is not a serious matter, for the internal resistance is high, and thus the current obtained on short-circuit is comparatively small. The rapid recovery of Weston cells after short-circuit is illustrated in Figs. 182 and 183, which shows results obtained by F. E. Smith.‡ Fig. 182 refers to a cell which was short-circuited for one minute, and Fig. 183 to one that was short-circuited for five minutes. The cell which was short-circuited for one minute was correct within a ten thousandth of a volt one minute afterwards, but 40 minutes were required for its recovery to 1 part in 100,000. The other cell was nearly

* *Phil. Trans.*, Vol. CLXXV., p. 411, 1884.

† *Proc. Roy. Soc.*, Vol. LXII., p. 117, 1897.

‡ *Phil. Trans.*" (A), Royal Society, Vol. CCVII., p. 393, 1908.

1 part in 1,000 low one minute afterwards; at the end of a second minute it was low by 1 part in 2,000, and after five minutes it had recovered within 1 part in 5,000. About $1\frac{1}{2}$ hours were required for its complete recovery.

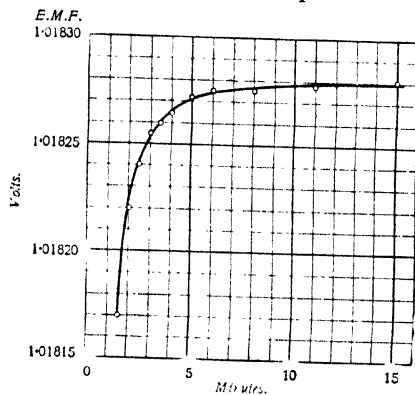


FIG. 182.—Recovery Curve of Cell short-circuited for 1 minute.
(F. E. Smith.)

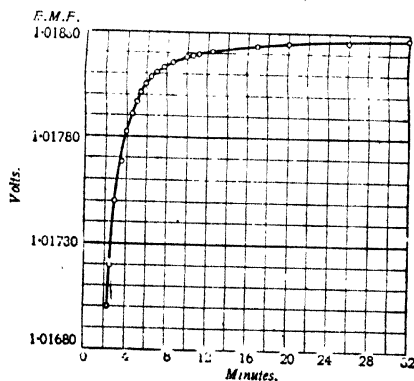


FIG. 183.—Recovery Curve of Cell short-circuited for 5 minutes.
(F. E. Smith.)

Similar results have been given by P. I. Wold,* and the subject has also been investigated by S. J. Barnett.†

Standard cells are not often used on circuits requiring an appreciable current. It is, however, sometimes convenient for the purpose of calibration to be able to put such a cell direct on to a galvanometer used as a voltmeter. In such a case the cell must be large so as to avoid polarisation, and this method can be used only for galvanometers of high resistance, the latter also being large in comparison with the internal resistance of the cell. The behaviour of standard cells when supplying a current has been studied by R. Threlfall and A. Pollock,‡ and by H. Tinsley.§

In accurate measurements it is necessary to know the temperature with some exactness, unless the temperature coefficient is very small. On that account, cells should be placed in a water bath if the terminal wires do not become immersed, or in an oil bath if the cells are of the ordinary H-form. It should, however, be borne in mind that it is useless to go in for refinements of measurement in one quantity if corresponding refinements cannot be carried into the measurement of every other quantity which is involved in the experiment to the same extent. For example, if the value of an E.M.F. is to be determined by reference to a standard cell, it is useless to determine the temperature to a higher degree of accuracy than that corresponding to the accuracy to which the E.M.F. of the cell is known, having regard to its variation with temperature. But in certain cases it may be necessary to make more careful corrections. For example, it may be required to compare one cell with another: here we may desire to know whether there is a very small difference, irrespective of whether we can accurately determine the whole value of either E.M.F. in itself.

* *Physical Review*, Vol. XXVIII., p. 132, 1909.

† *Physical Review*, Vol. XVIII., p. 104, 1904.

‡ *Phil. Mag.*, 5th Series, Vol. XXVIII., p. 353, 1889.

§ *The Electrician*, Vol. XLVII., p. 991, 1901.

The importance of the Weston cell as a *practical* standard cannot be over estimated, but the cell must not be regarded as being more than a convenient means of producing a commercial standard in terms of the volt. Considering the many processes which have to be undertaken to produce such a standard, on which nearly all measurements of current, voltage and power now depend, the achievement is remarkable. A word of caution is, however, necessary to those who use the cell for accurate work, such as the checking of meters, on which the financial returns of electricity supply undertakings depend. In such work there should be a systematic and periodical check on the standard cell by the use of at least three or four cells which may be checked against each other so as to detect any secular change. Probably no cell is perfectly constant, and experience shows that both Clark and Weston cells tend to fall in voltage, so that a serious error may result after several years if no such precautions are taken.

In such secular changes impurities no doubt play an important part. Mr. H. Tinsley informs the Author that he has for years held the view that impurities in cadmium sulphate may be carried over after two or three recrystallisations and may have an important effect on the E.M.F. of the Weston cell, apparently due to traces of iron and other metals. So far, English manufacturers do not appear to have produced a sufficiently pure zinc sulphate.

HELMHOLTZ STANDARD CELL.

Some attempts have been made to produce a cell whose E.M.F. should be exactly 1 volt, with the idea that such a cell would be more convenient than one having an E.M.F. which is not a round number. The practical advantage, however, does not really amount to very much, for the E.M.F. can only be exactly 1 volt at one particular temperature. A cell of this kind, containing chlorides instead

of the usual sulphates, appears to have been first described by Helmholtz. The E.M.F. is only approximately 1 volt, but may be adjusted by varying the density of the electrolyte. This use of an unsaturated solution is not objectionable so long as a cell is perfectly sealed, but if evaporation is possible a change in the E.M.F. necessarily occurs.

Carhart found that 16 per cent. increase in the density of the zinc chloride solution produced 3.5 per cent. decrease in the E.M.F., and that the density should be 1.391 at 15 deg. to give 1 volt. It therefore appears that an error in the density does not cause a correspondingly large error in the E.M.F. Carhart* gives the following description of the cell: "In the bottom of the tube is pure mercury in contact with a platinum wire; on this a paste of mercurous chloride and the zinc chloride solution; a cork diaphragm follows, holding the mercury and paste firmly in position, especially with some asbestos packing under the cork; zinc chloride is then added to the proper depth, and an amalgamated zinc rod, supported by a cork, completes the electrical combination of parts. The cell must be hermetically sealed as usual. Such a cell is perfectly portable and gives promise of long life. Its internal resistance is about 1,500 ohms, and it does not appear to suffer permanent change by heating to 50°C. or even to 60 deg." The cells also appear to be capable of giving constant results, mention being made of one cell which had maintained its E.M.F. for six years.

The chief advantage of this cell lies in the fact that the temperature coefficient is small. Carhart gives the following equation between the E.M.F. and temperature:—

$$E = 1 + 0.000094 (t - 15).$$

It will be noticed that the coefficient is positive, whereas that of the Clark cell is negative.

The Helmholtz cell has also received attention from W. Hibbert, who obtained satisfactory results. A difficulty

* *American Journal of Science*, Vol. XLVI., p. 60, 1893.

arises in the purification of the zinc chloride owing to the impossibility of crystallising the salt. This property of non-crystallisation is an advantage in the cell itself, because changes in density caused by solution and crystallisation do not take place, but this convenient method of purification has to be replaced by one that is less definite. It is found sufficient to warm the zinc chloride solution with zinc foil, which precipitates cadmium or other electro-negative metallic impurities and at the same time effects neutralisation. The specific gravity of the solution in the cell should be nearly 1.38. The zinc should be of good quality and amalgamated. The mercury and mercurous chloride should also be pure.

There appears to be no difficulty in securing good agreement between these cells, and they do not suffer from secular change, if properly sealed, at least in three or four years. The internal resistance is about 500 or 600 ohms, and the value of the temperature coefficient is stated by Hibbert to be about 0.000085 volt per degree.

Owing to the development of the Weston cell, it is improbable that the Helmholtz cell will receive further consideration at the hands of physicists.

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Adams and R. E. Day* found that light is also capable of producing an E.M.F. in selenium itself.

GENERAL PROPERTIES OF SELENIUM.

Selenium was discovered in 1817 by Berzelius in the deposits from sulphuric acid chambers. It is closely akin to sulphur in many of its properties, and, like that element, it exists in several allotropic modifications. The information given on this point in text-books is not very dependable, and we shall, therefore, rely upon a careful investigation of the more chemical properties by A. P. Saunders.† According to this investigator, selenium exists in the three following forms: (1) Vitreous and amorphous, (2) red crystalline, perhaps in two closely allied forms, and (3) grey crystalline, or metallic, which is conducting. The first two classes are non-conducting. In the three following paragraphs the properties of these modifications are given in detail.

VITREOUS AND AMORPHOUS SELENIUM.—If any variety of selenium is heated above 220°C ., it forms an ordinary liquid, but if this is cooled quickly it becomes more and more viscous, remaining soft even below 60°C .; but at 30°C . to 40°C . it becomes hard, and is then known as *vitreous selenium*, having a conchoidal glassy fracture. In its plastic condition it may be drawn into long threads, which are transparent and of a ruby colour by transmitted light.

If selenium is deposited from an aqueous solution of selenious acid (for example, by passing a current of sulphur dioxide through the solution) a precipitate is obtained which, when dry, forms an impalpable powder without any trace of crystalline form. This is known as *amorphous selenium*.

* *Proceedings*, Royal Society, Vol. XXV., p. 113, 1876.

† *Journal of Physical Chemistry*, Vol. IV., p. 423, 1900.

Vitreous selenium gives a red streak on paper. When powdered it is grey; but if powdered very fine it becomes red, and is then indistinguishable from the red amorphous selenium.

If amorphous selenium is warmed to 40°C. it darkens and coagulates to a soft mass, which, on cooling, becomes hard and brittle, assuming somewhat the features of the vitreous form.

Apparently the vitreous and amorphous varieties differ only in the state of aggregation. It is found that liquefied selenium is slightly soluble in carbon bisulphide. Also, freshly precipitated amorphous selenium under certain conditions is soluble in water, and is then known as soluble selenium. This property, however, is lost with the lapse of time.

The vitreous form is quite stable by itself at ordinary temperatures, and is the form in which selenium is ordinarily sold.

The specific gravity of amorphous selenium is 4.26 and of vitreous selenium 4.28.

RED CRYSTALLINE SELENIUM (non-conducting).—

This variety separates from solutions in carbon bisulphide, or it may be obtained by allowing the vitreous or amorphous form to stand in carbon bisulphide, or some other solvents, at ordinary temperatures. Saunders is of the opinion that it is probably able to exist in two different forms, both belonging to the same crystal system and both soluble in carbon bisulphide. There are indications of an unstable melting point at 217°C. The specific gravity of red crystalline selenium is 4.28.

GREY CRYSTALLINE SELENIUM (conducting).—

The grey crystalline, or metallic, form is obtained from the other varieties by heating, and in the presence of certain

liquids this change takes place even at ordinary temperatures. This variety may be regarded as the stable form of selenium, into which the other forms tend to pass, being stable at all temperatures up to the melting point, which is 217 deg. The other forms are unstable, the red crystalline being intermediate between the grey crystalline and the vitreous. Although it is a simple matter to change from the two other varieties into the grey crystalline, Saunders was unable to bring about a change in the reverse direction.

It has been noticed by some observers (notably by Saunders) that quinoline and some kindred organic bodies have the property of converting amorphous selenium, at least superficially, into the metallic form.

Selenium is polymorphous, the form of the crystals depending on the conditions in which they are produced. F. C. Brown* has obtained a number of different forms by vaporising selenium and allowing it to condense on a cool surface. All these were conductors of electricity, and all but one were doubly refracting. Some crystals are soluble in carbon bisulphide and some are insoluble.

The specific gravity of grey crystalline selenium is 4.80.

ELECTRIC CONDUCTIVITY.—The resistivity is high, being of the order of 2×10^{16} ohms per centimetre cube in the dark; but the figure varies enormously, according to the mode of preparation and with the value of the applied P.D.

There has been some discussion as to whether the conduction is simply metallic or whether it is electrolytic in its character. In support of the electrolytic view there is the fact that the resistance is generally found to vary with the applied pressure; in other words, the resistance does not simply follow Ohm's law, but decreases in proportion to the P.D. when this is small, the original state being slowly regained when the pressure is removed. The propor-

* *Physical Review*, Vol. IV. (2nd series), p. 85, 1914.

tional and the lag are noticeable in Fig. 184, which is due to L. S. McDowell.* Moreover, after a current has been flowing, it is found that the selenium is polarised; but, unlike the corresponding phenomenon in electrolysis, the E.M.F. of polarisation, according to Luterbacher,† is in the same sense as the current by which it is produced; in other words, the polarisation current flows in the same direction as the current that has been applied, instead of in the inverse

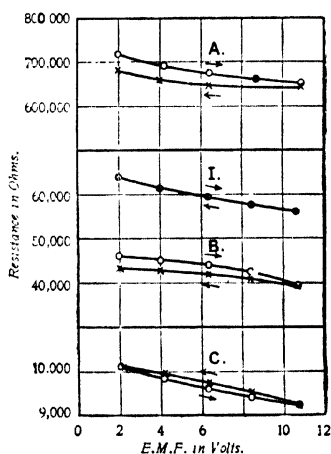


FIG. 184.—Variation of Resistance of Selenium with applied P.D. (McDowell).

direction. If this is the case, the polarisation so produced differs essentially from what is generally meant by this term. On the other hand, W. G. Adams and R. E. Day‡ found that the polarisation was in the opposite direction to the current by which it was produced, just as in electrolysis. Measure-

* *Physical Review*, Vol. XXIX., p. 1, 1909.

† *The Electrician*, Vol. LXVII., p. 736.

‡ *Proceedings, Royal Society*, Vol. XXV., p. 113, 1876.

ments by the Author were found to support this view, and showed the E.M.F. of polarisation, unless it falls off rapidly, to be very small.

The variation of resistance with the applied pressure, as observed by J. Luterbacher,* is very large, as seen in Fig. 185, and to fall off considerably at the higher voltages. The curve is approximately a parabola. Alternating current produces the same effect, but not to such a marked degree. This is shown in Fig. 186. Possibly the smaller effect at the

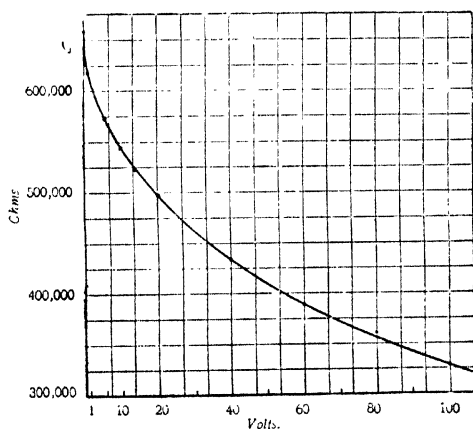


FIG. 185.—Variation of Resistance of Selenium with Applied P.D. (Luterbacher).

higher pressures may be due to the fact that a steady state is reached more slowly with high than with low pressures: the creeping is greater, as pointed out by Ries.† Any heating up of the selenium by the passage of the current would also lower the resistance, but it is pointed out by

* *Loc. cit.*

† *Annalen der Physik*, Vol. XXXVI. p. 1,055, 1911; *Science Abstracts*, 1912, No. 1428.

Lutembacher that the effect of such heat would be least with small currents, whereas the reduction of resistance is more marked with the smallest currents than with larger currents. A curve showing the heat produced is given in Fig. 186.

E. E. Fournier d'Albe* has shown that the variation in the resistance for all pressures above 1 volt is proportional to the logarithm of the voltage. The observations in one case were carried beyond 100 volts.

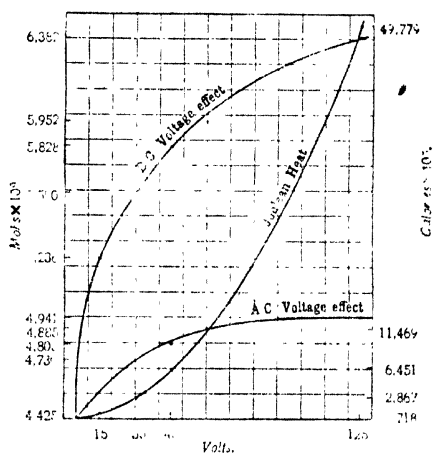


FIG. 186.—Comparison of Continuous and Alternating Pressures as affecting the Resistance of Selenium (Lutembacher).

On the other hand, V. Chiarini† found that the P.D. required to cause a current to flow varied from as low a value as 0.02 up to 0.9 volt; and A. H. Pfund‡ found that certain old selenium resistances failed to show polarisation, even when the applied pressure was as high as 110 volts.

* *Proceedings*, Royal Society, Vol. LXXXVI, p. 452, 1912.

† *Atti*, Accademia dei Lincei, Vol. XVIII., p. 246, 1909; *Science Abstracts*, 1909, No. 884.

‡ *Physical Review*, Vol. XXVIII., p. 324, 1909.

A. Pochettino* states that if the primary current is not applied for more than two minutes the initial intensity of the secondary, or polarisation, current increases with the voltage applied and with the square root of the time of application. The polarisation currents continue for a considerable time. Thus, taking the case of the application of 54 volts, the secondary current was $1,100 \times 10^{-9}$ ampere seven seconds after the primary current ceased, and was still 8×10^{-9} after 2,010 seconds.

By allowing the selenium to discharge through a galvanometer immediately after cutting off the applied pressure polarisations were observed by Luterbacher† varying from 7 to 22 millivolts. Assuming that the galvanometer was of high resistance, this shows a very small E.M.F. of polarisation, but possibly its value falls very rapidly. In any case, we cannot look upon polarisation as an explanation of the fall in resistance, for it would have to reach an extraordinarily high value to produce any noticeable effect with applied pressures of 100 volts.

It seems difficult to accept an electrolytic view of the conductivity, because we are dealing with a single element, unless selenium is capable of splitting up into two ions which are identical chemically, but which differ electrochemically, one being electro-positive to the other.

The conductivity between an electrode and selenium is to some extent unilateral.‡

F. C. Brown§ has shown that mechanical pressure causes an increase in conductivity. A resistance of 96,000 ohms at atmospheric pressure was reduced to 63,000 ohms at a pressure of 218 kg. per square centimetre, the pressure being applied hydraulically.

* *Nuovo Cimento*, Vol. XVI., p. 381, 1908; *Science Abstracts*, 1909, No. 693.

† *Loc. cit.*

‡ Chiarini, *loc. cit.*

§ *Physical Review*, Vol. IV., p. 85, 1914.

It has been pointed out by both Giltay and F. C. Brown* that the conductivity is increased by abrasion; for example, by filing. The selenium recovers its original condition after about a month.

Selenium generally has a positive temperature coefficient of resistance. Rieß† distinguishes two forms of crystalline selenium, which he terms α and β . The α modification has a negative temperature coefficient, and is obtained by heating up to temperatures below 200°C. (the transformation being most complete by prolonged heating at 195°C.), followed by rapid cooling. The β modification has, within certain limits, a positive temperature coefficient, and is obtained by heating at temperatures above 200°C.

THE EFFECT OF LIGHT.

LIGHT-POSITIVE SELENIUM.—The usual effect produced by increasing the illumination of crystalline selenium is a diminution of resistance. Generally the comparison is made between what may be termed the “dark resistance” (*i.e.*, the resistance of the selenium when all light is excluded) and the resistance when the illumination has some definite value.

The effect obtained is illustrated by the curves in Fig. 187. From these it is seen that the change in conductivity is not instantaneous; it is at first rapid and proportional to the time of exposure, but it very soon becomes slower and slower until a steady state is reached. Hours may be required for the steady state to be attained. This time lag is known by the name of inertia. Although two selenium resistances may have the same sensitiveness (*i.e.*, they may ultimately change in conductivity to the same extent on exposure to a given illumination), they may differ materially in lag, so

* *Physikalische Zeitschrift*, Vol. XIII., p. 859, 1912; *Science Abstracts*, 1913, No. 232.

† *Physikalische Zeitschrift*, Vol. IX., p. 228, 1908; *Science Abstracts*, 1908, No. 1,294.

that the effect of a given illumination for a brief period may be very different. Lag is more apparent in recovery than in excitation.

A feeble illumination produces its full effect less rapidly than a strong illumination. For example, Pfund gives the figures 3 minutes and 15 seconds respectively for two such cases. In considering these matters it must be borne in mind that these observations refer to selenium in thin layers.

When the light is removed or reduced the selenium proceeds to recover its initial conductivity, but here, again, the

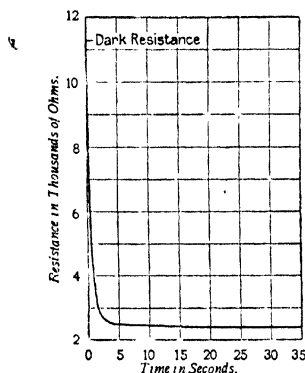


Fig. 187.—Variation of Resistance with Time of Exposure (Torda).

effect is not instantaneous. In fact, recovery curves are characterised by a slower action than the excitation curves, a fact which is illustrated in Fig. 188. The time of recovery generally increases with both the intensity and the duration of the excitation, and for this reason long exposures are avoided, as far as possible, where selenium is used for practical purposes.

Prolonged exposure sometimes causes a diminution of the effect first produced. This has been observed by F. C. Brown*

* *Physical Review*, Vol. XXXIII, p. 1, 1911.

in the case of resistances made by Giltay (of Delft, in Holland). Such curves are reproduced in Fig. 189. Generally, however, prolonged exposure has no such effect.

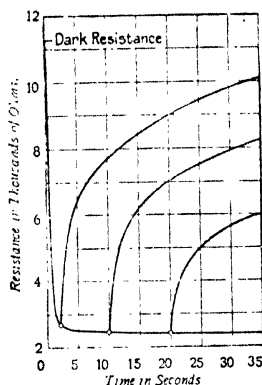


FIG. 188.—Variation of Recovery with Time of Excitation (Torda.)

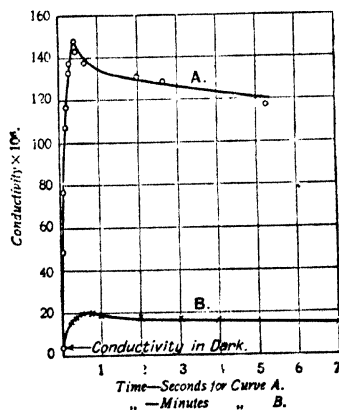


FIG. 189.—Effect of Prolonged Excitation in the Case of Giltay Resistances (F. C. Brown).

LIGHT-NEGATIVE SELENIUM.—Although the effect of increased illumination is generally to give increased conductivity, the reverse effect has been observed. So far, the method of producing the negative variety of selenium is not well understood. F. C. Brown* has found that such selenium can be obtained by placing the amorphous variety in a mercury vacuum until it becomes black, after which it is pressed between electrodes. Even at atmospheric pressures this change takes place if selenium is held over heated mercury. It does not seem to be due to the absorption of mercury vapour. This method of producing a superficial conducting film was discovered many years ago by R. J. Moss,† and may be carried out either *in vacuo* or by placing the selenium in mercury.

The properties of light-negative selenium have been studied by Lilah B. Crum.‡ Although the general effects observed were simply the inverse of those shown by light-positive selenium, they were characterised by great unsteadiness and uncertainty. For example, cases were found in which both positive and negative results were obtained from the same resistance alternately within a period of a few minutes.

Negative effects have also been observed by A. Pochettino and G. C. Trabacchi.§

LIGHT - NEUTRAL SELENIUM.—A. Knothe|| found that when sublimed selenium was exposed to sulphur dioxide gas it became a very good conductor, but was insensitive to light.

* *Physical Review*, Vol. II., p. 153, 1913.

† *Chemical News*, Vol. XXXIII., p. 203, 1876.

‡ *Physical Review*, Vol. XXXIII., p. 538, 1911.

§ *Nuovo Cimento*, Vol. XIII., p. 286, 1907; *Science Abstracts*, 1907, No. 1561.

|| *Elektrotechnische Rundschau*, Vol. XXI., p. 23, 1903; *Science Abstracts*, 1904, No. 152.

DEPENDENCE ON WAVE LENGTH.—It was very soon discovered that, generally speaking, the part of the spectrum including the yellow-red rays is more effective in its photo-electric effect on selenium than any other. The curves reproduced in Fig. 190, and which are due to A. H. Pfund,* are typical. From these curves it is seen that the maximum is very marked for wave-lengths of about 0.7μ , and do not vary much for the different illuminations examined. In making such an investigation it is necessary to be sure that the same energy is received at all observation

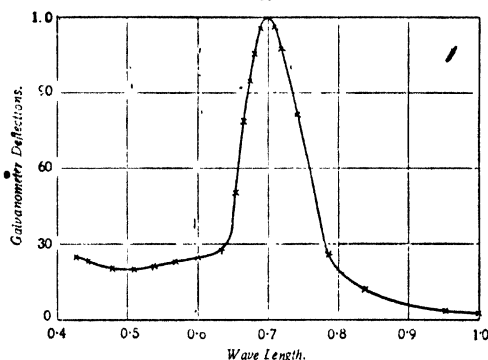


FIG. 190.—Curves showing Variation of Effect with Wave Length (Pfund).

points in the spectrum. This is ensured by first receiving the illumination at each point on a thermopile and varying the illumination until the same deflection is obtained for each point.

Later investigations, however, have shown that the above statement must be accepted with considerable reservations. The same author† has shown that under feeble illuminations

* *Physical Review*, Vol. XXVIII, p. 324, 1909.

† *Physical Review*, Vol. XXXIV., p. 370, 1912; *The Electrician*, Vol. LXX., p. 337, 1912.

a maximum may occur in the greenish-yellow. This is seen from the curves in Fig. 191. Here the ordinates show the galvanometer deflections obtained for each of four illuminations, which were in the ratio 1 : 4 : 9 : 16. For the lowest illumination (Curve I.) the maximum is in the greenish yellow, but when the illumination is increased four times the maximum shifts to the red. It is noticeable that all

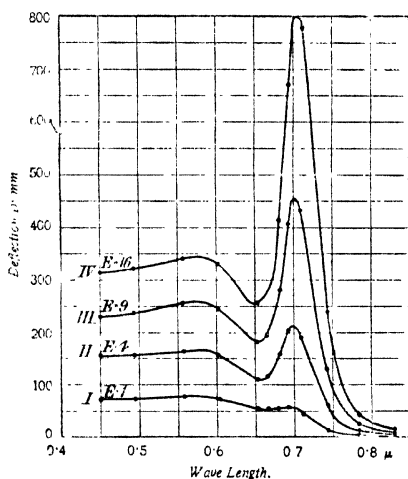


FIG. 191.—Variation of Position of Maximum with Intensity of Illumination (Pfund).

the curves show two maxima. This is a feature which is very generally found.

E. O. Dieterich* has shown that the position of the maximum depends upon the temperature at which the selenium is annealed. If the temperature is high the maximum sensitiveness is in the blue, but if the temperature is lower the maximum tends to shift to the red. Some

* *Physical Review*, Vol. IV., p. 467, 1914.

curves illustrating this fact are given in Fig. 192. In the view of Dieterich, there are two types of crystal, one sensitive to red and the other to blue rays. If the temperature is too high for the formation of crystals which are sensitive

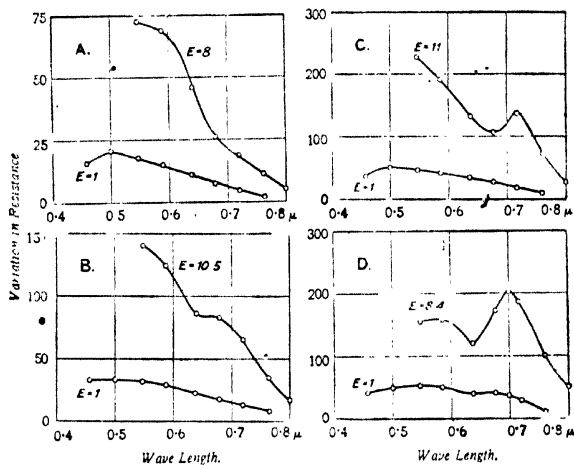


FIG. 192.—Curves showing Variation of Position of Maximum with Temperature of Annealing (Dieterich).

Applied pressure, 16 volts; exposure, 0.4 second.

- A. Resistance heated at 210°C. for four hours immediately after making.
- B. Resistance heated at 210°C. for one hour and then at 200°C. for four hours.
- C. Resistance heated at 210°C. for 30 minutes and then at 190°C. for six hours.
- D. Resistance heated at 210°C. for 30 minutes and then at average temperature of 170°C.

to red, the maximum is in the blue. Various mixtures of the crystals would lead to the maximum being at some intermediate point.

It is natural to suppose that these differences of sensitive-

ness with wave-length might be accompanied by differences in absorption and reflection of corresponding wave-lengths by the selenium. Thus, if the light effect is due to penetration of the light, we should expect that when selenium is sensitive to, say, blue light it would show a maximum of absorption and a minimum of reflection for light of that wave-length. A. H. Pfund,* however, did not find any corresponding maximum and minimum in the absorption and reflection curves respectively corresponding with the maximum in the light sensibility curve. Absorption was found to be more marked in the blue and fell off towards the red, irrespective of sensitiveness.

In all these properties there is liable to be a variation from cell to cell, as might be anticipated, owing to differences in the details of preparation.

LAW OF VARIATION OF LIGHT EFFECT.—The following formula has been given by E. Ruhmer†:—

$$R_d/R_l = (l/d)^n,$$

in which R_d and R_l are the value of the resistance under the smaller and brighter illuminations d and l respectively. The value of n was found to vary between 0.25 and 0.35.

Roughly, the variation in resistance when a steady condition has been reached varies as the square root of the illumination, but when the illumination is either very short or very feeble it is directly as the illumination.

G. Athanasiadis prefers the more exact statement that

$$i = G(G - a)b,$$

in which i is the illumination, G is the conductance and a, b are constants.

* *Physical Review*, Vol. XXVIII., p. 324, 1909.

† *Elektrotechnische Zeitschrift*, Vol. XXV., p. 1021, 1904; *Science Abstracts*, 1905, No. 808.

‡ *Annalen der Physik*, Vol. XXV., p. 92, 1908; *Science Abstracts*, 1908, No. 671.

P. J. Nicholson* found that the change in conductivity varied as a power of the illumination, or as I^n , the value of n varying from 1 to $\frac{1}{2}$ according to the conditions, being $\frac{1}{2}$ for long exposures.

In all such formulæ it is evidently necessary to define the experimental conditions rather carefully. This fact is brought out by the curves in Fig. 193, which are due to Pfund.† Here the law is expressed in the form $D=KE^B$, in

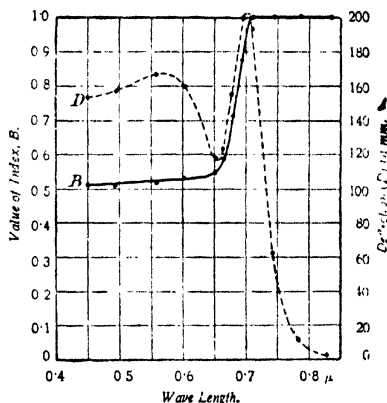


FIG. 193.—Curve showing Variation in B in Formula $D=KE^B$ with Wave Length.

Illumination, 2.1 metre candles; exposure, $12\frac{1}{2}$ seconds.

which D is the deflection of the galvanometer, K is a constant, E is the energy received per unit area (in this case 2.1 metre-candles) and B is a number. With equal energy in different parts of the spectrum, curve D shows the deflections obtained, and curve B gives the corresponding values of B if this simple formula is to hold. It appears that

* *Physical Review*, Vol. III., p. 1, 1914.

† *Physical Review*, Vol. XXXIV., p. 370, 1912; *The Electrician*, Vol. LXX., p. 337, 1912.

B is about $\frac{1}{2}$ for wave-lengths shorter than 0.65μ and 1 for wave-lengths greater than 0.7μ . Consequently, the exponent must vary with the quality of the light.

SENSITIVENESS. — The sensitiveness of a selenium resistance to light may be expressed in the form

$$(R_d - R_l) \div R_d,$$

or

$$(G_l - G_d) \div G_d,$$

in which, for a given illumination, R_d and R_l are the values of the resistance when the selenium is in the dark and illuminated respectively, and G_d , G_l are the corresponding conductances.

The sensitiveness falls off at very low temperatures. For example, Pochettino* mentions a case in which the resistance fell from 31,000 to 18,000 ohms at ordinary temperature and from 2,600 to 1,900 ohms at the temperature of boiling liquid air; that is, the sensitiveness fell from 0.42 to 0.2. On the other hand, the sensitiveness decreases with rise of temperature at ordinary temperatures, and is stated by Pochettino† to be a maximum at -40°C .

L. S. McDowell‡ states that changes due to light take place more slowly at low temperatures, but that the final change carried to the point of saturation is enormously greater. The sensitiveness is also much greater at low temperatures.

It is sometimes said that the sensitiveness, expressed as the ratio of the conductivity in the light to that in the dark, varies from, say, 5 up to 20, and even 200. This basis gives information in a form in which it is often desired, but such figures do not convey a true meaning unless they are

* *Atti, Accademia dei Lincei*, Vol. XI., p. 286, 1902; *Science Abstracts* 1902, No. 1,888.

† *Nuovo Cimento*, Vol. VI., p. 147, 1911; *Science Abstracts*, 1911, No. 920.

‡ *Physical Review*, Vol. XXXI., p. 524, 1910.

obtained under definite conditions. Unfortunately, high sensitiveness is only obtained along with high resistance; in fact, the lower the resistance the lower the sensitiveness, which fact limits the usefulness of selenium for many purposes. When, for instance, the action required is the working of a relay, it is not so important to know the "sensitiveness" of the Se as it is to know the additional current it will yield under a given illumination, or what may be called its "efficiency."

STANDARD TESTS.—There are so many possible variables in estimating this efficiency that E. E.

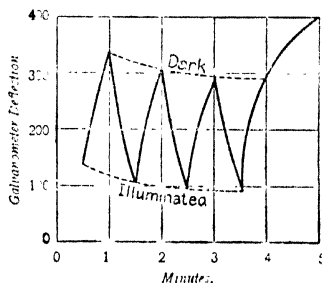


FIG. 194.—Galvanometer Deflection with Alternate Periods of Darkness and Illumination.

Fournier d'Albe* has suggested the following standard conditions for testing:—

- (a) *Quality of Light*.—Complete radiation from a standard pentane lamp.
- (b) *Illumination*.—To be 1 lux—i.e., 1 metre-candle.
- (c) *Applied Pressure*.—To be 1 volt.
- (d) *Temperature*.—To be 15°C.
- (e) *History*.—If the variation of conductivity is determined from the total recovery it will vary

* *Proceedings, Royal Society*, Vol. LXXXIX., p. 75, 1913.

according to the previous immediate history of the selenium. In order to avoid this, the selenium is exposed alternately to light and darkness for one minute in each period until the galvanometer shows steady deflections for the light and dark conditions. Curves similar to those in Fig. 194 are thus obtained.

- (f) *Measurement*.—Two Galvanometer readings are taken at two successive minutes during recovery. Taking the initial reading (the last one under illumination) as zero, the variation in the reading after one minute in the dark as d_1 , and the variation after two minutes as d_2 (see Fig. 195), then the total variation from the light condition up to complete recovery may be calculated from the formula

$$\left. \begin{array}{l} \text{Total variation in} \\ \text{conductance} \end{array} \right\} = \frac{d_1 d_2}{2d_1 - d_2}.$$

The efficiency may be stated in micro-mhos per lumen,* or (with a pressure of 1 volt), in micro-amperes per lumen, or micro-amperes per square centimetre of sensitive surface divided by 0.0001.

The above conditions are laid down more particularly for feeble illuminations; for other classes of work it might be desirable to modify them. The efficiency so obtained refers to exposures for one minute. If the selenium is to be used for shorter or longer intervals of exposure, the time interval in the measurements would be correspondingly altered.

The efficiencies observed may be as high as, say, 25,000 micromhos per lumen for very feeble illumination, falling to, say, 5,000 or even a few hundred micromhos per lumen.

Similarly, the efficiency of a selenium cell would be defined as the E.M.F. in volts generated per lumen when the illu-

* A light source of 1 c.p. gives a flux of 4π , or 12.566, lumens.

mination on the plate is 1 lux (1 metre-candle). In the case of the cells used by G. M. Minchin for the selenium photometry of stars the efficiency was 1,270 volts per lumen.

Fournier d'Albe* states that selenium as a detector of light is at least 100,000 times as sensitive as a potassium

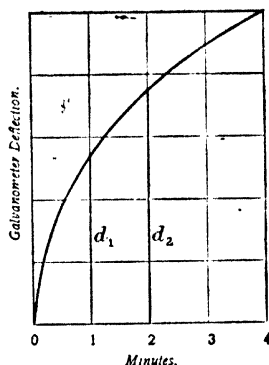


FIG. 195.—Calculation of Total Recovery.

photo-electric cell. Compared with the eye, selenium has the advantage of being more sensitive when the light is diffused.

DEPTH OF PENETRATION.—There has been some discussion as to the depth to which the light penetrates the selenium. F. C. Brown† has shown that the effect of light is not restricted merely to the part that is illuminated; the effect is also observed at some distance. He concluded that the depth of effective penetration was about 0.014 rpm. On the other hand, W. S. G ripenberg‡ is of the opinion that the action extends deeply into the interior.

* *Loc. cit.*

† *Physical Review*, Vol. V. (2nd series), p. 167, 1915; and Vol. XXXIV., p. 201, 1912.

‡ *Physikalische Zeitschrift*, Vol. XV., p. 462, 1914.

ELECTRIC WAVES.—It is worth while to note that a variation in the resistance of selenium occurs when it is exposed to electric oscillations. Interesting work in this direction has been done by Louise S. McDowell.* It appears that the effect is somewhat erratic; it may be immediate or it may be deferred, depending on the state of the selenium. Possibly the effect may be akin to the well-known coherer action that is produced on metallic powders by electric waves.

In this connection it may be mentioned that Fritts† has found an increase in the sensitiveness of selenium to be caused by transmitting alternating currents through it, but the effect is liable to be transient.

THEORIES.

The theories which have been advanced to account for the action of light upon selenium may be classed broadly as electrolytic, chemical (or physico-chemical) and electronic.

The difficulty in proposing any theory is that there are so many facts to be explained, many of them somewhat contradictory.

The electrolytic theory was proposed by Shelford Bidwell,‡ who considered that the action was due to selenides formed by the interaction of the selenium and the metal support. Bidwell showed that such a theory would account for the effect of annealing, the diminution of resistance with the applied voltage, the largeness of the resistance temperature coefficient, the observed reduction of resistance with time and certain other phenomena. This theory, however, is disproved by the fact that when carbon or graphite is used as a support, so that selenides cannot be formed, and the selenium is carefully purified, it is still

* *Ibid. cit.*

† *Electrical Review (Telegraph Journal)*, Vol. XVI., p. 208, 1885.

‡ *Philosophical Magazine*, Vol. XX., p. 178, 1885.

sensitive to light. Also, pure selenium has been found to be more sensitive than the impure element.

In chemical theories it is assumed that the selenium consists of two or more allotropic modifications, one modification changing into another under the influence of light, and the reverse change taking place when the illumination is removed or reduced. R. Marc* has reached the conclusion that there are two allotropes, which he terms A and B. In heating up selenium the change from A to B takes place most readily at 200°C. The establishment of equilibrium is facilitated by the presence of metallic catalytic agents, such as silver and platinum. This point of view has also been studied by A. Pochettino.†

The physico-chemical theory is based upon the idea that the effects are due to crystalline structure, to orientation of the crystals or differences in pressure between their faces. Work in this direction has been carried out by E. O. Dieterich,‡ and by L. P. Sieg and F. C. Brown,§ though the last named inclines to an electron theory. Sieg and Brown have shown that the sensitiveness of a selenium crystal varies on the application of mechanical pressure to the crystal, and that both the sensitiveness and the position of the maximum in regard to wave-length may vary according to the crystalline axis along which the incident beam passes.

That the pressure between the crystals may explain the phenomena to some extent is supported by the fact that electrical oscillations cause variations in the resistance (as already mentioned), and are, of course, of the same nature as light.

* *Zeitschrift für Anorganische Chemie*, Vol. XLVIII, p. 393, 1906; *Science Abstracts*, 1906, No. 1111.

† *Nuovo Cimento* Vol. IV., p. 189, 1912; *Science Abstracts*, 1913, No. 233.

‡ *Physical Review*, Vol. IV. (2nd Series), p. 467, 1914.

§ *Physical Review*, Vol. IV. (2nd Series), p. 507, 1914; and Vol. V. (2nd Series), p. 167, 1915.

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* *Ibid. cit.*

† *Electrical Review (Telegraph Journal)*, Vol. XVI., p. 208, 1885.

‡ *Philosophical Magazine*, Vol. XX., p. 178, 1885.

tional ions at any time, I the illumination and a a constant, then

$$dN/dt = I - aN^2.$$

A steady state is reached when $I = aN^2$, showing that the final change is proportional to the square root of the illumination, which is found to be the case. Integrating, we have

$$N = \sqrt{I/a} \tanh(t\sqrt{I/a}),$$

$$\text{or} \quad t = \frac{1}{2\sqrt{I/a}} \log \frac{N_0 + N}{N_0 - N},$$

in which N_0 is the final addition of ions, or final increase in conductivity. The recovery curve is given simply by

$$dN/dt = -aN^2,$$

$$\text{or} \quad \frac{1}{N} - \frac{1}{N_1} = at,$$

in which N_1 is the additional conductivity at the moment of cutting off the light. If the galvanometer deflection at this moment is called zero, and d_1, d_2 are two readings taken at equal time intervals after that moment, then

$$N_1 = \frac{d_1 d_2}{2d_1 - d_2}.$$

We have already referred to this formula, which gives the total recovery. That there should be any remaining conductivity in the dark is due to thermal agitation; complete re-combination of the ions would only take place at the absolute zero of temperature, and would take an infinite time.

The above ionisation theory does not account for the behaviour of selenium under strong illumination, which is probably complicated by heat effects.

CONSTRUCTION AND PRACTICAL APPLICATION.

SELENIUM RESISTANCES.—Since the resistivity of selenium is high, it is desirable to adopt some form of con-

struction in which the selenium bridge between the two electrodes is as short and as wide as possible. Further, the layer of selenium must be thin, because the light action takes place only near the surface, and therefore the resistance cannot be diminished by increasing the depth of the cross-section, otherwise the sensitiveness is diminished. On the other hand, it seems undesirable to have extreme thinness.

Perhaps the simplest form of construction is that adopted by Pfund.* A piece of ground glass, say 1 cm. \times 3 cm. \times 0.1 cm. thick is used as the support. The glass is warmed so that a stick of selenium melts when rubbed on it, and a layer is thus obtained thin enough to appear red by transmitted light. The crystalline grey metallic variety forms at once. Around this is wound four strands of No. 30 I.W.G. copper wire. The ends of two of these (say Nos. 1 and 3) are then fixed, and the remaining two are removed. This leaves a spiral of two wires separated from each other.

The final step is to anneal the selenium so that it is in the required crystalline condition throughout. This is effected by placing the device in an air bath at 180°C. for about five minutes. The resistance is then about 20 megohms, and if it is exposed to the light of a 16 c.p. lamp at a distance of 30 cm. the resistance falls to about one-ninth of this value. Since moisture renders the conductor non-permanent, it should be covered with a piece of glass, or mica, fixed with a little wax. Or Ruhmer's method may be followed, and the resistance sealed in a vacuum tube.

A similar method is to wind on two insulated wires side by side, and to remove the top of the insulation so as to leave the wires exposed at the top, but with insulation between them. If the wire is insulated with enamel it is easy to remove the insulation; but if it is insulated with silk, the latter requires treating with a varnish that will stand the

* *Physical Review*, Vol. XXVIII., p. 324, 1909.

somewhat high temperature of the subsequent treatment (for example, varnish made from synthetic resins*). The silk can then be removed with a fine file or with sand paper. One difficulty in this method is to obtain an even surface, the tendency being for some of the wires to be higher than the others. This difficulty is most easily overcome by winding on a tube instead of on a flat surface, but the resulting patch of selenium is then not so effective, owing to curvature.

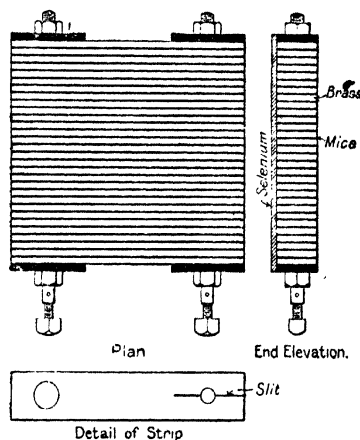


FIG. 196.—Details of Support for Selenium Resistance.

A more complicated construction is adopted by F. Townsend,† and is shown in Fig. 196. A block is built up of alternate strips of brass and mica. The alternate plates of brass are connected together, one set to one terminal and one to the other. One face of the block is then coated with selenium.

* Obtainable from the Damard Lacquer Co., of Birmingham.

† *The Electrician*, Vol. LIII, p. 987, 1904; *Electrical Review* (New York), Vol. XLV., p. 391, 1904.

At one time it was thought necessary to anneal for a long time and to cool down very slowly from the annealing temperature. This, however, does not seem to be the case.

When the selenium is first applied it is in the vitreous condition, and appears like a black mirror. If, however, the temperature conditions are correct this will change rapidly to the crystalline form, and the surface will then appear grey, sometimes with a reddish or purple tinge, and matt in character. As a source of heat, a piece of sheet iron below which is the flame of a bunsen burner is convenient. If difficulty is experienced in obtaining the transformation, this may be effected by heating for 10 minutes in an oven (preferably electric for convenience) at 180°C.-190°C.

The final value of the resistance depends upon the heat treatment that is given. This is shown by the figures in Table XIII., due to E. O. Dieterich.*

Table XIII.—*Effect of Different Annealing Temperatures.*

No. of resistance.	Temp. of annealing.	Period of annealing.	Resistance, ohms.
23	210°C. — 200°C.	6 hours	233,000
22	210°C.	4 "	358,000
28	210°C.	5 "	490,000
16	180°C.	3½ "	1,400,000
15	190°C.	2 "	3,690,000

The figures in Table XIV. show that if the cells are heated for only a short time at a high temperature and then annealed at a lower temperature the resistance is much less than if the short treatment at the higher temperature is omitted. Thus, Nos. 18 and 19 received the same treatment, except that No. 18 had a preliminary heating at a higher temperature for half an hour; yet its resistance was one-fortieth that of No. 19. When using a 16 c.p. lamp at a distance of 30 cm. the sensitiveness of the above varied from 5/1 up to 20/1.

* *Physical Review*, Vol. IV. (2nd series), p. 467, 1914.

Table XIV.—Effect of Different Annealing Temperatures.

No. of resistance.	Temp. of annealing.	Period of annealing.	Resistance, ohms.
18	{ 210°C. 180°C.	{ $\frac{1}{2}$ hour 9 "	978,000
19	{ 180°C. 210°C.	{ 9 " $\frac{1}{2}$ "	40,000,000
20	{ 210°C. 180°C.	{ $\frac{1}{2}$ " 14 "	250,900
21	{ 180°C. 180°C.	{ 14 " 14 "	9,500,000

Various metals can be used as electrodes, but copper has the objection that it oxidises when heated. Nickel is better in this respect, and is said to be as satisfactory as platinum. Also resistance wire, such as platinoid, seems preferable to copper, and has the advantage over nickel that it can be easily obtained silk covered. Films of graphite have also been effectively used as a conducting base.

E. Ruhmer* draws a distinction between hard and soft resistances, the difference being dependent on the allotropic modification of the selenium that is obtained. A "hard" resistance is obtained by rapid cooling after applying the selenium to the electrode, the resistance being agitated during cooling. A "soft" resistance is obtained by cooling the selenium slowly after applying it to the electrode; it is then heated for a time to 200°C. The soft resistances are of higher conductivity than the hard resistances, and are more sensitive to weak, but less sensitive to strong, illumination than hard resistances.

Fig. 197 shows a Giltay resistance made by P. J. Kipp & Zonen, of Delft (Holland), from which it is seen that these well-known resistances are of the wire type. The wire is of platinum-iridium, the working surface being 4.6 cm. \times 2.6 cm. Two types of these resistances are made, namely, low resistance and high resistance. It is stated by the makers that the former has a dark resistance of about

* *Physikalische Zeitschrift*, Vol. III., p. 468, 1902; *Science Abstracts*, 1903, No. 89.

10,000 ohms, and a small sensitiveness of, say, 5 for diffuse daylight (*i.e.*, ratio of dark resistance to light resistance); the latter has a dark resistance of 200,000 to 500,000 ohms, or more, and a sensitiveness of 50 or 60. A 32 c.p. lamp at a distance of half a metre appears to be taken as the equivalent of "diffuse daylight." The above values illustrate the fact that low resistance and high sensitiveness do not go together.

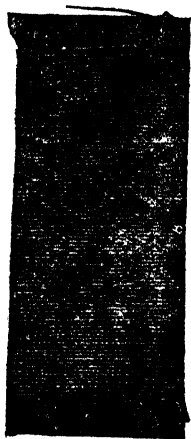


FIG. 197.—Giltay Selenium Resistance (full size),
made by Kipp & Zonen.

Messrs. Kipp state that selenium resistances sometimes fail through internal short circuits. In their opinion this is due to high voltages from the breaking of inductive circuits. Consequently, if such a resistance forms part of an inductive circuit it is advisable to short-circuit the resistance before the circuit is broken.

SELENIUM CELLS.—Turning to selenium cells, we find that much less work has been done in this direction than on selenium resistances. This is probably due to the fact that

a cell is less robust than a resistance. The internal resistance of such a cell is necessarily very high, and therefore the generation of a small E.M.F., such as 1 volt, loses a good deal of its effectiveness. With selenium resistances, on the other hand, the low value of the conductivity can be compensated considerably by applying a high voltage.

Selenium cells appear to have been first used by R. Sabine.* He used selenium on platinum wire as one electrode and platinum foil as the other, the electrolyte being distilled water. In the dark the selenium was found to be electro-positive to the platinum (about 0.1 volt), whereas in the light it became electro-negative (about 0.05 volt). This effect diminished after a few minutes, but the selenium still remained electro-negative until the light was cut off, when the original state was regained.

G. M. Minchin† used selenium cells in astronomical photometric measurements. As electrodes, or supports for the selenium, he found that platinum, silver, tin, zinc and bismuth gave considerable results; copper gave nearly a zero E.M.F.; and the best results were obtained with aluminium. Platinum was used for the other plate and methyl alcohol as the electrolyte except in the case of aluminium, when acetone was found to be the best. The E.M.F. was about 0.25 volt. The greatest sensitiveness was obtained in the yellow part of the spectrum, though the variation with wave-length was not nearly so marked as in the case of selenium resistances.

Recently experiments with selenium cells have been described by A. A. C. Swinton.‡ Copper was used as the support for the selenium, the uncovered parts being varnished with enamel. The other plate consisted of a metal or carbon having a hole cut in it of the same size as the layer

* *Nature*, Vol. XVII., p. 512, 1878.

† *Philosophical Magazine*, Vol. XXXI., p. 207, 1891.

‡ *Proceedings*, Physical Society of London, Vol. XXVII., p. 186, 1915.

of selenium on the copper. The cell was mounted in a glass vessel, with tap water as an electrolyte (since acid or alkali caused the selenium to strip), so that light could be projected through the inactive electrode on to the selenium. A zinc electrode was found to be electro-positive to the selenium, and it became still more electro-positive when the latter was illuminated. On the other hand, with carbon or copper, the selenium was the electro-positive element, becoming electro-negative on illumination. These results are similar to those of Sabine with platinum.

APPLICATIONS.

The most serious practical application of selenium resistances has been in the telegraphic transmission of pictures. For this purpose, light is passed through the picture, which is kept moving; the transmitted light therefore varies with the shading of the picture, and as it is allowed to fall upon a selenium resistance, currents are transmitted over the telegraph line which vary according to the shading of the picture. At the receiving end this fluctuating current causes variations in a beam of light which falls upon a sensitive film moving in synchronism with the picture at the transmitting end.

In order that such a method should work at all quickly it is necessary to eliminate the lag to which the selenium resistances are subject, and to have a constant current as the result of a given illumination irrespective of the time of exposure. This has been ingeniously effected by A. Korn,* by connecting two selenium resistances, as in Cardew's method of measuring resistances, as indicated in Fig. 198. Since the current through the galvanometer is the difference between the currents through the selenium resistances, it follows that if the resistances were precisely similar in their

* *The Electrician*, Vol. LVIII., p. 577, 1907. See also T. Thorne Baker, *The Electrician*, Vol. LXIV., p. 1070, 1910.

response to light no current would flow as the result of illumination. If, however, the resistances differ suitably in their sensitiveness and inertia, a given illumination will always cause the same effect. The result will be independent of previous illumination, because if one resistance tends to be, say, too low the other resistance will have the same tendency, and since the two effects are in opposition they tend to cancel. Actually the compensating resistance is illuminated slightly later than the one to be compensated, so that compensation does not come into play immediately on exposing the operating resistance. In practical working the place of the galvanometer is taken by the line and the receiving instrument.

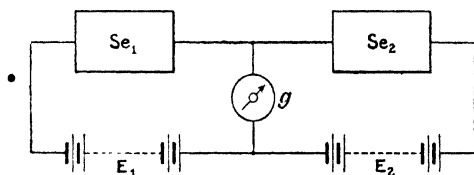


FIG. 198.—Compensation of Selenium Resistances.

Many attempts have been made to use selenium in photometric work, so as to eliminate the eye in such work and render the measurements less dependent on the skill of the observer. At the outset it must be recognised that, selenium photometers can only be produced by calibration against lamps of known candle-power, and since the sensitiveness of selenium varies with the wave-length of the light, the indications obtained will depend on the quality of the light. Consequently such instruments can only be relied upon for comparing lamps of the same character as the standards with which they are calibrated.

A selenium photometer for industrial use has been described by T. Torda.* In this instrument the current through

* *The Electrician*, Vol. LVI., p. 1042, 1906. •

the selenium when in circuit with two dry cells is read on a milliammeter. Having read the current corresponding to the dark resistance a shutter is opened so as to expose the selenium to the source of light it is decided to measure, this being at a fixed distance. In order to have definite conditions, the shutter is controlled by clockwork, so that it remains open for only two seconds, and then remains closed for 40 seconds before a further observation can be made. In this way long exposures are avoided and a sufficient period of darkness is given to ensure a reasonable degree of complete recovery. The candle-power is read from a calibration curve.

The earliest practical application of selenium was made by Graham Bell * in his photophone, an instrument for telephonic transmission by means of light. In this device the voice was directed against the back of a mirror, and a beam of light reflected from the front of the mirror was directed on to a selenium resistance, in series with which was a telephone receiver and a battery. The effect of the voice was to cause variations in the beam of light, or to give what Bell termed an "undulating beam," to which the selenium responded, and thus the telephone reproduced the transmitted sounds.

An apparatus termed the optophone, depending upon selenium, has been devised by E. E. Fournier d'Albe † to enable the blind to read ordinary type. In this apparatus a beam of light passes through a rotating wheel having holes perforated on a number of concentric circles. Thus, a number of intermittent beams are obtained, each having a different frequency. These beams are focussed on the paper in a space the size of a letter of the print to be read, and are diffusely reflected from the paper on to a selenium resist-

* *American Journal of Science*, Vol. XX., p. 305, 1882.

† *The Electrician*, Vol. LXXII., p. 102, 1913; and *Proceedings Royal Society*, Vol. XC., p. 373, 1914.

ance, in series with which is connected a battery and telephone relay, the latter being connected to an ordinary telephone receiver. If the paper is white a note is heard in the telephone corresponding to the resultant of all the beams, but if the paper bears a letter, a certain number of the beams are ineffective, being no longer reflected, and the note changes. Consequently, if a line of print is passed over the aperture where the beams are focussed the note varies with the letter, and with practice the print can be read by the sounds that are emitted.

Many proposals have been brought forward to work devices by relays actuated by light falling on selenium. Most of these have been rendered useless by the inconstancy of the selenium resistances used, and their high temperature coefficient of resistance. The most successful application so far has been to light buoys anchored in waters difficult of access, the light being automatically switched on at nightfall. A similar application is the automatic switching on and off of street lamps. Mr. C. J. Turner, electrical engineer to the Hoylake Urban District Council, has used selenium for this purpose.* The selenium resistance, which varies from 3,000 ohms in the light to 150,000 ohms in the dark, is placed across the supply voltage in series with a wire resistance of 14,500 ohms, and the coils of an electromagnet. In daylight the current is sufficient to cause the electromagnet to pull over an armature fixed to a lever. The latter carries a forked contact piece, which dips into mercury cups, and completes the lamp circuit. Consequently when the lever is raised by the action of the electromagnet the lamp circuit is broken. At night the current becomes so far reduced that the armature is released. The exact point of switching in is regulated by adjusting a weight which more or less balances the lever.

* *The Illuminating Engineer*, Vol. IX., p. 85, 1916.

CHAPTER XIII.

CARBON-CONSUMING CELLS AND THE COMMERCIAL GENERATION OF ELECTRIC ENERGY.

Efficiency of Generation, p. 415.—Electric Lighting by Primary Batteries, p. 418.—Cost of Generation, p. 420.—Conditions Necessary for Success, p. 423.—Carbon as an Electro-Positive Material, p. 424.—Influence of Efficiency on Cost of Generation, p. 424.—Voltaic Difficulties with Carbon, p. 426.—Position of the Oxidising Agent, p. 428.—Gas Cells, p. 432.—Borchers' Cell, p. 435.—C. J. Reed's Method, p. 437.—Utilisation of Free Carbon, p. 440.—Jacques' Cell, p. 441.—Blumenberg's Cell, p. 445.—Short's Cell, p. 446.—Heating of Cells, p. 447.—Jungner's Cell, p. 448.—Emission of Electricity from Hot Carbons, p. 450.

EFFICIENCY OF GENERATION.—On account of the inefficiency, complication, and cost of steam plant, attempts have been frequently made to supply electrical energy from primary batteries on a commercial scale. That there is some ground for the hope of economy appears from the fact that the all-day efficiency of a steam-driven generating plant on a lighting load is not likely to be more than 6 per cent., *i.e.*, only 6 per cent. of the energy in the coal appears as electrical energy.* A station with plant of the Diesel type shows, of course, a higher efficiency. Also power stations, which are more efficient than those for lighting, need scarcely be considered in this connection.

In a steam-driven plant there are several transformations of energy, but in a battery there is only one such transformation, and consequently there is the possibility of a greater efficiency. We start with the energy of a chemical reaction; and the question to be dealt with is:

* *Proc. Inst. Junior Engineers*, Vol. IX., p. 97, 1899.

How much of this energy can be converted into electrical energy? To this question it is difficult to give an answer which shall have a general application, because the efficiency varies with the class of battery considered, but it is possible to arrive at a figure having a more or less mean value for commercial purposes.

The causes of inefficiency in a battery are the following:—(1) Temperature-coefficient; (2) Polarisation; (3) Internal resistance; (4) Local action; (5) Incomplete utilisation of materials.

Let us consider the efficiency in the case of a large battery such as would be necessary for a central station; for example, a battery of 100 cells, giving 100 volts, and capable of supplying 1,000 amperes, and required for lighting purposes. A low value is taken for the E.M.F., because that of a carbon-consuming cell is not likely to be much greater than one volt.

(1) *Temperature-Coefficient*.—As we have already seen, the E.M.F. of a cell is not given merely by the heat of formation of the salt voltaically formed. There is a term depending upon the temperature-coefficient which may be positive or negative, and therefore the E.M.F. may be greater or less than the equivalent of the heat of formation. In other words, the efficiency may be greater or less than 100 per cent., according as the temperature-coefficient is positive or negative. Consequently, in seeking a general figure for the efficiency of a battery, it is preferable to disregard temperature-coefficients, and thus to assume 100 per cent. efficiency on that head.

(2) *Polarisation*.—The loss due to the polarisation is a variable one, increasing with the current density and therefore with the load. Since a cell to be of commercial value for this class of work must have good depolarising qualities, it may be assumed that the drop on account of polarisation at full load will not exceed 15 per cent. Assuming further that the average load in a lighting station is about one

quarter of the maximum in a day's run, then the mean loss is about 4 per cent., or the efficiency 96 per cent.

(3) *Internal Resistance*.—In the case of internal resistance the loss again increases with the load. Assuming that each cell has an internal resistance of 0.0002 ohm, then the resistance of the whole battery would be 0.02 ohm and the drop in pressure when supplying a current of 1,000 amperes would be 20 volts. It may seem that there is no particular reason for assuming such a value for the internal resistance, but the assumption is only tantamount to a statement that the internal resistance must not much exceed this figure if the plant is to be commercially successful. If a quarter of this loss be again taken as a mean value the loss will amount to 5 per cent., or the mean efficiency to 95 per cent.

(4) *Local Action*.—The loss per hour due to local action is probably a fairly constant quantity, being much the same whether the battery is on open circuit or is supplying a current. But the ratio of material wasted to that which is usefully dissolved varies from an infinite value when the cell is on open circuit to very possibly a negligible quantity at full load. It is difficult to fix upon a definite figure because local action varies very much with the nature of the battery; but it is probable that the loss might be reduced to 5 per cent., more particularly when it is remembered that a battery of the kind considered would not be subject to intervals of rest. We shall therefore assume an efficiency of 95 per cent.

(5) *Utilisation of Materials*.—The loss due to incomplete utilisation of materials is generally serious. Plates, as a rule, cannot be completely dissolved because a certain mechanical strength is required to maintain the desired form: further, the corrosion is seldom uniform, with the result that parts, or even the whole, of a plate may drop off while still in good condition. It is also often impossible to completely utilise the electrolyte owing to the fall in E.M.F. as chemical changes proceed. On a large scale

the waste material could no doubt be worked up to some extent for further use, and in such a case it may perhaps be assumed that the loss would not exceed 15 per cent.

For the total efficiency of the battery we have therefore the following figures :—

Cause of Inefficiency.	Efficiency, per cent.
Temperature Co-efficient.....	100
Polarisation	96
Internal Resistance	95
Local Action	95
Incomplete utilisation of Materials	85
Total Efficiency.....	73.6

It appears, then, that we have a possible efficiency of about $73\frac{1}{2}$ per cent. for a battery, as compared with 6 per cent. for the corresponding steam plant. There is therefore cause for encouragement as far as efficiency is concerned, but unfortunately the cost per unit does not depend merely upon efficiency; it depends also very largely upon the cost of the material or fuel consumed, upon handling and maintenance—a fact which is too frequently forgotten by inventors of primary batteries.

ATTEMPTS AT ELECTRIC LIGHTING BY PRIMARY BATTERIES.—Numerous attempts were made during the years 1886—1888 to use primary batteries for the commercial generation of electrical energy. Among the most promising may be mentioned the Lalande* battery, containing the usual copper oxide as a depolariser in a caustic alkali solution, and Upward's† battery, in which the plates were carbon and zinc, the latter being in a porous compartment filled with chlorine.

Coming to more recent years, in 1898 the Rowbotham battery received a good deal of public attention. The negative plates are of carbon, while the positive plates are

* *The Electrician*, Vol. XVII., p. 281, 1886.

† *The Electrician*, Vol. XVII., p. 153, 1886.

iron, which has the advantage of being cheaper than zinc, but in some respects is more difficult to use. The cells are of somewhat complicated construction. They consist of an open central compartment with an air-tight compartment on either side. The latter are connected by means of porous porcelain tubes through which there pass carbon rods; these are connected together and form the negative plate, the iron plates being placed in the open part of the cell. The closed compartments contain a mixture of sulphuric acid (for example, to the extent of 30 per cent.), water, and a little nitric acid, whilst the open compartment is filled with water only. Sufficient acid finds its way through the porous tubes to render the water conducting. When the circuit is closed, gas is evolved at the carbon rods, and gives rise to pressure in the closed compartments, with the result that more acid is forced through the tubes, thereby reducing the internal resistance and enabling the cell to discharge at a higher rate. In batteries the cells are mounted on an incline, with all the closed compartments communicating in such a way that the electrolyte flows from cell to cell and is thus maintained of a sufficient strength. Similarly a stream of water is supplied to the open compartments in groups. When the current generated is diminished, the pressure in the closed compartments also diminishes, with the result that less acid passes through to the iron. Finally, when current is no longer taken from the battery the open compartments are automatically flushed out with water, thus reducing local action to a minimum on open circuit. The E.M.F. per cell is 1.35 volts, and the cost per unit, excluding depreciation, interest on prime cost, or superintendence, is stated by H. T. Harrison to be under 5d. per Board of Trade unit, but this figure probably does not include the cost of handling materials and manufacture of plates.

In 1898 there also appeared Doe's battery, the essential feature of which is the electrolyte; the composition of

this has not been disclosed. According to a report by H. F. Parshall, the E.M.F. is very constant on closed circuits

Later, there appeared Benko's battery, which is described in Chapter VIII. of this volume.

COST OF GENERATION.—The following figures are of interest as showing the cost of production which has been claimed for various systems of primary batteries:—

Battery.	Cost as stated.
Ross.....	= gas at 3s. 6d.
Regent.....	= gas at 6s.
Upward.....	= gas at 7s.
Weymersch.....	= 0.75d. per 30-watt lamp hour.
Renard.....	= 0.2d. per c.p. hour
O'Keenan.....	= 0.5d. per 12 c.p. lamp hour.
Holmes and Burke.....	= 0.5d. per 10 c.p. lamp hour.
Newton.....	= 0.16d. per 10 c.p. lamp hour.
D'Humy.....	= 0.25d. per 10 c.p. lamp hour.
Rowbotham.....	= 5d. per B.T. unit.

Many of these figures appear at first sight to be very favourable, but it must be remembered that they probably refer only to cost of material, or include profit on possible bye products, and are therefore liable to be very misleading.

Let us consider for a moment what is the minimum theoretical cost of materials. Most batteries employ zinc as the positive plate, the cost of which in the raw state at the present time (November, 1901) is about £17 per ton. Now, the amount of zinc required to furnish 1,000 ampere hours, according to the electrochemical equivalent, is 2.67lbs.; and therefore if the mean terminal potential difference of a cell is 1 volt, a Board of Trade unit will require 2.67lbs. of zinc, the cost of which at this wholesale price is 4.86d. If the mean terminal pressure is 1.5 volts the cost of this item falls to 3.24d., and if the pressure is 2 volts the cost is only 2.43d., the cost varying inversely as the mean terminal pressure at which the cell can be worked.

As an example of the complete calculation of the minimum cost of materials, we may take the Daniell cell, in which the reactions are exceptionally definite. Besides zinc, we have zinc sulphate, copper sulphate, and copper. Of these, zinc sulphate only requires to be supplied in the

first instance, being subsequently formed by the action of the cell, solution being withdrawn and water added occasionally to prevent saturation. This salt may therefore be neglected. Copper sulphate, on the other hand, must be continually supplied, but it gives rise to pure deposited copper, which may be sold. The E.M.F. of a Daniell cell is, roughly, 1.1 volts; we may therefore take 1 volt as a possible mean terminal pressure when on circuit.

The amount of copper sulphate, considered as having the formula $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, decomposed by 1,000 ampere hours is 10.13 lbs., which, at the rate of £22 per ton, costs 23.50d. Similarly, the amount of copper deposited by 1,000 ampere hours is 2.57 lbs., which, at the rate of £72. 10s. per ton for "best selected," has a value of 19.96d. Thus we have the following figures for the cost of a Board of Trade unit generated by a Daniell cell, with a mean terminal pressure of one volt :—

Minimum Theoretical Cost of Materials per B.T.U. Generated by a Daniell Cell.

Material.	Weight.	Cost in Pence.
Zinc	2.67 lbs.	4.86
Copper Sulphate.....	10.15 "	23.50
		<hr/>
Less copper deposited	2.57 "	28.36
		19.96
		<hr/>
		Total 8.40

Consequently the cost of material per Board of Trade unit, excluding impurities, local action, and handling, and at wholesale prices, is 8.40d. If the terminal working pressure were 2 volts, this figure would, of course, be reduced to one-half the above. But even if such were the case, it is necessary to remember that no account has been taken of maintenance, interest on capital, and labour, in addition to handling (including manufacture of plates), local action, and impurities, which have already been mentioned. Consequently, the cost per unit is much higher than the cost

by steam generation. It is not, however, necessary that the cost per unit should be as low as with steam plant, for there are many isolated private installations where the simplicity of a primary battery would be welcomed if the cost of generation were not excessive.

Such calculations show the importance of high E.M.F. in a cell. Another point is also important, viz., the cost may depend to a large extent upon the electrolyte; in other words, the high cost of zinc is not such a controlling factor as is sometimes thought. As a cheaper material than zinc, iron has sometimes been used; but it has the great disadvantage that if it is placed in an acid solution local action cannot be prevented, and if the electrolyte is not acid, oxide or basic salts are deposited.

Instead of basing costs on theoretical figures, which are liable to lead to results that are far too low, it is better to rely on actual experiment as far as possible. As the result of numerous tests, the author came to the conclusion that the amount of zinc required in a Benkö battery,* assuming careful working, was about 3.24 lb. per unit, including local action and waste. The prices of materials (wholesale, in 1910) may be taken as follows: Amalgamated zinc plates, about £34 per ton; sodium bichromate, 3d. per lb.; concentrated sulphuric acid, £3. 2s. 6d. per ton, or more dilute acid, £1. 10s. per ton. The author found that the quantities and costs were approximately as follows on the assumption that the waste zinc amounted to about 25 per cent. and would be re-sold at, say, £1. 10s. below the market price (£22 per ton) of raw zinc:—

	Per unit.
Zinc, 3.24 lb. at 3.65d.....	11.8d.
Less 0.81 lb. at 2.2d.	1.8d.
	10d.
Sodium bichromate, 3.6 lb. at 3d.	11d.
Sulphuric acid, conc., 9 lb. at 0.33d.	3d.
	Total 24d.

* *Journal, Institution of Electrical Engineers*, Vol. XLVI., p. 741, 1911.

Cost of carriage would, of course, have to be added for each particular case and also the cost of labour. The latter would be very small if proper facilities were provided, as a solution of the kind used is made very quickly.

The problem of supplying light from primary batteries is much more important now than it was some years ago, because the conditions have changed. Low voltage metal filament lamps consuming only 1 watt per candle are available in convenient sizes, and comparatively high candle power low voltage lamps, consuming only half a watt per candle, or thereabouts, are coming on the market. Consequently, the number of units used for a given illumination per annum is very much less, and thus a cost of 2s., or even 2s. 6d., per unit is not by any means prohibitive for small country houses which are not large enough to warrant the installation of an oil engine set and battery of accumulators. For example, 200 units per annum at 2s. per unit amounts to £20, which, in many cases, would not be considered an exorbitant sum to pay for light in the principal rooms of a small country house.

NECESSARY CONDITIONS.—In addition to being cheap, the positive material should be as highly electro-positive as possible and coupled with a strongly electro-negative material in order that the E.M.F. may have a high value. A sufficient difference in electro-chemical character is sometimes obtained by using a compound, such as an oxide, for the negative material: for example, lead is not nearly so electro-positive as zinc, yet it gives a high E.M.F. when coupled with lead peroxide in sulphuric acid, the peroxide acting at the same time as a depolariser.

If the negative material undergoes no appreciable change its cost may be relatively high without rendering the cell commercially useless from the point of view of cost. But if a voltaic change takes place, such as reduction by a polarising ion, then the material must be either cheap

or easily regenerated. This remark also applies to the electrolyte.

CARBON AS AN ELECTRO-POSITIVE MATERIAL.—

The search for a cheap material has naturally led to the consideration of coal for this purpose. Coal has the advantage of cheapness, and, although it is practically a non-conductor on account of the hydrocarbons which it contains, it is readily carbonised and thus converted into a conducting material which is nearly as good from the point of view of energy, and gives rise in its carbonisation to valuable by-products. Nearly all our power at the present time is derived from the combustion of coal, but in a manner which is far from efficient. In this process the carbon may burn either to carbon monoxide, with a heat of combustion of 29,000 calories, or to carbon dioxide with a heat of 96,960 calories. The latter is the maximum heat obtainable by the complete combustion of carbon, but of this heat, as already stated, only about 6 per cent. is converted into electrical energy by steam plant for lighting. If we could carry out this combustion, or oxidation, voltaically, then it would be possible to rise from this low efficiency, to a very much higher figure, which we estimated on p. 418 to be $73\frac{1}{2}$ per cent. If the process were limited to the use of carbon monoxide instead of carbon, completing the oxidation from carbon monoxide to the carbon dioxide, then the efficiency of $73\frac{1}{2}$ per cent. would be reduced to $51\frac{1}{2}$, but the gain would still be very considerable. Before dealing further with this possibility, which has been the dream of many an inventor, let us return to the question of efficiency.

INFLUENCE OF EFFICIENCY ON THE COST OF GENERATION.—

In considering the effect of an increase of efficiency on the cost of generation we shall regard coke (or carbon) and coal as being practically equivalent. They are not strictly so, because the calorific value of coke is not as high as that of the best coal; but, on the other hand, coke

is somewhat cheaper, with the result that the cost is about the same for both kinds of fuel for the same calorific effect.

Now, if it were possible to pass from an efficiency of 6 per cent. to $73\frac{1}{2}$ per cent., then about twelve times the number of units could be generated for the same quantity of coal, and the coal bill would be reduced to one twelfth. Let us consider what is the effect of a saving of this kind. It may be assumed that a unit can be generated with steam plant and distributed for lighting by the combustion of 10 lb. of coal, and that, if the price of coal is 17s. per ton, the cost per unit (including maintenance) amounts to about 2.5d. In this figure the coal accounts for 0.9d., and if this can be reduced to one-twelfth the saving per unit amounts to over three farthings. This is a substantial saving, being at the rate of over 30 per cent. for the supply authority, but it does not affect the price to the consumer to the same extent, because the latter price must always exceed the cost price by an amount sufficient to pay interest upon the capital invested. If the price to the consumer is to be much reduced, then it will be necessary in some way to diminish the capital required. Economy in this direction might be possible in the generating station, but is otherwise limited on account of the heavy outlay on distributing systems, the cost of mains under existing conditions accounting for something like half the capital expenditure in small undertakings, as distinct from large systems, to which these remarks do not apply. Voltaic methods would not produce a saving in the mains.

It is easy to see what would be the effect of an increased efficiency in the case of steam plant, but it by no means follows that the same result would be gained by effecting this economy voltaically. Whether the increased efficiency would lead to greater economy must depend upon the battery itself. Capital expenditure, cost of materials, maintenance and labour must all be taken into consideration; and when that is done it is, unfortunately, quite

possible that we should find, in the case of a carbon-consuming battery, that, although the efficiency is much improved, the total cost is increased instead of being diminished.

VOLTAIC DIFFICULTIES WITH CARBON.—In attempting to make use of carbon as the electro-positive material in a voltaic cell, theoretically we are not limited to any particular kind of reaction. If it were possible, we might, for instance, attempt the voltaic conversion of carbon into a salt; but since the question of cost is of paramount importance, and since oxygen is the element which is most readily obtained, and of which we have an inexhaustible supply, it is usual to limit the problem to the voltaic *oxidation* of carbon.

In considering this problem, with its many difficulties, it is necessary to clearly bear in mind the distinction already referred to between chemical and voltaic action (see p. 8), and, further, the fact that local action may sometimes be obtained, but that it is useless for our purpose. It should also be remembered that voltaic reactions take place between *ions*.

One of the earliest attempts to obtain electrical energy direct from carbon was that of Jablochkoff, who placed carbon in fused potassium nitrate. But such a method cannot produce any result of value, for the oxidation takes place quite as energetically whether the electric circuit is opened or closed. Having regard to the local action which arises, when impure zinc is placed in sulphuric acid, it might be objected that local action on open circuit does not preclude the possibility of obtaining electrical energy on closing the circuit, although the method might thereby be rendered commercially useless. But the local action between zinc and sulphuric acid takes place through the agency of the ions; it is essentially electrolytic. There is no reason, on the other hand, to look upon the

oxidation of carbon by potassium nitrate as electrolytic. The ions of KNO_3 are K and NO_3 . But the oxidising power of KNO_3 depends upon its reduction to potassium nitrite, or KNO_2 , from which decomposition KNO_3 appears as $\text{KNO}_2 + \text{O}$. The oxidation, therefore, does not take place by means of the ions, and it is unlikely that there should be any transformation into electrical energy. As another example of this kind sulphuric acid may be mentioned. This acid can be reduced by suitable reactions to sulphurous acid, showing that it may be looked upon as $\text{H}_2\text{SO}_3 + \text{O}$, but it does not follow that these are the ions. On the contrary, the ions of sulphuric acid are H and HSO_4 , or H, H and SO_4 , according to the conditions.

One of the first difficulties with which we have to contend is that of getting the carbon into solution. It is an element which is unacted upon by the usual solvents. This in itself does not necessarily render it impossible that voltaic solution should occur, for voltaic reactions often take place which are impossible by ordinary chemical means: in fact, this must be the case in every voltaic cell if local action is to be avoided. But it is necessary that solution should take place by means of ions and that the solution obtained should be an electrolyte, or, in other words, should be in a state of ionisation.

Unfortunately carbon does not form salts. When, for example, it is used as an anode in hydrochloric acid, it does not pass into solution as a chloride, and although a chloride exists—viz., carbon tetrachloride, CCl_4 —this has none of the properties of a salt, and is, moreover, an insulator. Indeed, comparatively few compounds of carbon are electrolytes; and in such as there are, carbon does not appear as an ion.

Another difficulty is due to the position of carbon in the electro-chemical series. As already pointed out, it is important that the positive plate of a cell should be highly electro-positive as compared with the negative plate

Unfortunately, carbon is itself strongly electro-negative. By referring to the table of elements given on p. 19 it will be seen that no suitable metals are electro-negative to carbon, from which it appears that recourse must be had to compounds of the metals with the non-metals to obtain a suitable material—for example, oxides. The electro-negative character of a body is generally increased by causing it to combine with a non-metal.

Recapitulating, we may say that the chief difficulties encountered in the voltaic consumption of carbon are on account of the following:—

- (1) The insoluble nature of carbon.
- (2) The scarcity of electrolytic carbon compounds.
- (3) The inability of carbon to act as an ion in such organic compounds as are electrolytes.
- (4) The electro-negative character of carbon.

POSITION OF THE OXIDISING AGENT.—Supposing that voltaic oxidation is possible, let us consider where the oxidising agent must be placed. In the case of a simple element, consisting of zinc and platinum in sulphuric acid, it is not essential that the zinc should be in contact with the acid. If the conditions are arranged so that the depolarisation is good, we may imagine zinc sulphate to be formed so rapidly on the surface of the zinc that the acid is there neutralised and is no longer in contact. In fact, the zinc may be placed in a porous pot containing zinc sulphate solution, the acid being only in the neighbourhood of the platinum. The current will still be generated, and thus we see that what we regard as the active solvent in the case of a simple element may be either in contact with the positive material or away from it. Is it also the case that the oxidising medium may be either in contact with, or away from, the carbon?

To answer this question, let us consider a few possible combinations. First take the case of carbon coupled with

a metal M in water, which for the moment we will suppose to be an electrolyte. The reaction may be represented as in Fig 199. An atom of carbon, being tetravalent, combines with four hydroxyls to give $C(OH)_4$. This compound is unknown, but may be looked upon as the hypothetical

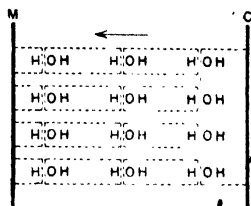


FIG. 199. — Hypothetical Voltaic Oxidation of Carbon in Water.

carbonic acid, H_2CO_3 , in combination with one molecule of water. The polarising ion is seen to be hydrogen, but after a time carbon would be deposited on M in the same way as it is possible to have deposition of zinc on the platinum of a simple element.

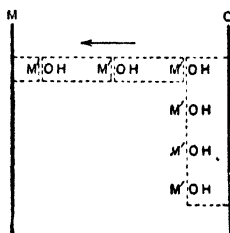


FIG. 200 — Oxidation by a Metallic Hydroxide.*

If the water is replaced by a metallic hydroxide, $M'OH$, as the electrolyte, the oxidation is then represented by Fig. 200. Here M' is the polarising ion, instead of hydrogen, and will have to be removed, unless it is the same as M .

In time carbon will reach the plate M, and will tend to be deposited, requiring further oxidation, though local action on the plate M will prevent such a deposition to a great extent. If the action is continued until the whole of the metal M' is replaced by carbon, we then have carbon as the exclusive polarising ion, as indicated in Fig. 201. The

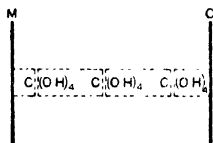


FIG. 201.—Carbon as the Polarising Ion.

action of the cell must then cease, unless oxygen is supplied at the plate M. In this case the cell is analogous to a gas cell, the oxidation taking place, as it were, twice—once at the carbon plate and again at the metal M.

In place of an oxidising electrolyte we may have a body, $M'A$, which is more like a salt, and acts merely as a

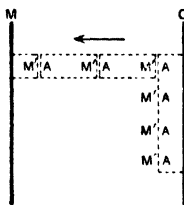


FIG. 202.—Solution but not Oxidation.

solvent, consisting of a metal M' , which we will suppose monovalent, and an electro-negative radicle A. This body must be such that carbon is able to form the body CA , in which case the voltaic reaction is represented by Fig. 202.

Here M' is the polarising ion; there is solution, but not oxidation. By transforming the cell into the Daniell type,

as indicated in Fig. 203, the hydroxide $M'OH$ being introduced in the neighbourhood of the plate M' , there is solution in one compartment and oxidation in the other. The oxidation of the carbon here takes place as the polarising ion, and the oxidising agent is at a distance from the carbon plate.

From the above considerations it appears that, theoretically, the oxidising agent may act simultaneously as the solvent and as the oxidant, or it may be placed at a distance from the carbon, acting as the oxidant alone and oxidising the carbon as the polarising ion. Provision must, of course, be made for depolarisation in any case, but the polarising ion is not necessarily carbon. In this

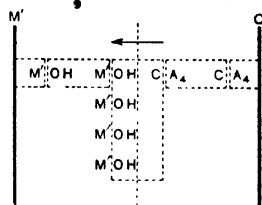


FIG 203.—Solution and Oxidation.

discussion we have assumed that carbon is capable of forming a carbonic acid which is an electrolyte. Unfortunately, this is not the case, any such acid (if formed) immediately breaking up into water and carbon dioxide gas.

In what precedes, the problem has been discussed from a perfectly general point of view. It will, however, be remembered that there are two possible main reactions. We may either attempt the oxidation of carbon to carbon dioxide; or, if that is impossible, the oxidation of carbon monoxide to the dioxide. It is unnecessary to consider the oxidation of carbon to the monoxide, partly because the thermal value of the reaction is too small to give a cell with a sufficiently high E.M.F. to be a commercial success,

and partly because if this reaction were possible it is probable that there would be no difficulty in completing the oxidation to the dioxide, and thus utilising the maximum energy available. We shall therefore consider only the two remaining reactions, turning first to the second alternative.

GAS CELLS.—What is usually known as Grove's gas cell consists of two platinum electrodes partly immersed in acidulated water and partly in gases—for example, one in hydrogen and the other in oxygen. Grove experimented with various other gases, besides oxygen and hydrogen, including carbon monoxide coupled with oxygen.

It appears that the effective action of such a cell depends upon the extent of the occlusion or absorption of the gases by the electrodes. Thus platinised platinum is more effective than ordinary platinum because it has a greater power of occlusion. We may therefore look upon the plates of an oxygen-hydrogen cell, for example, as consisting of oxygen and hydrogen, which are possibly in the atomic state and therefore in a very suitable condition for voltaic action.

The Grove gas cell is not of commercial value because the rate of occlusion of the gases is too small. As soon as the quantity of electricity required per second exceeds the equivalent of the rate of occlusion, the E.M.F. falls rapidly. The total occlusion, and therefore the capacity of the cell for a high rate of discharge, depends, of course, upon the area of the electrodes, especially on that part near the surface of the electrolyte; but the area required to give a discharge suitable for commercial purposes is so large as to be out of the question on account of the cost. It is therefore necessary to improve the character of the electrodes if there is to be any commercial development on these lines.

A considerable advance has been made by K. Siegl,* who holds the view that the immersed parts of the plates of a gas cell cannot be effective when the cell is in action, because the gas on that part of the surface cannot be easily renewed. Probably the most important part of the plate is the surface near the electrolyte. For his cells Siegl uses platinised lumps of carbon about 3 mm. in diameter, so as to avoid the cost of platinum sheet. These are placed in flat closed cells of unglazed earthenware, which form gas chambers, and which also contain carbon plates to act as collecting electrodes. The earthenware cells are placed in a vessel containing the electrolyte in which the cells become soaked, so that the carbon surfaces within are moistened. Any number of cells can be so arranged, alternately positive and negative, similar poles being connected together. By this arrangement a large junction is obtained between the upper surface of the electrolyte and the platinised carbon element.

Siegl tried chlorine, oxygen, air, carbon dioxide, acetylene, coal gas and hydrogen, the electrolyte being dilute sulphuric acid, except in the case of chlorine, when it was dilute hydrochloric acid. The following E.M.F.s were obtained :—

Chlorine and hydrogen	1.4 volta.
Oxygen and hydrogen	0.9 "
Air and hydrogen	0.8 "
Air and coal gas	0.7 "
Carbon dioxide and hydrogen	0.8 "
Air and acetylene	0.3 "

It is difficult to see what reaction there can be with carbon dioxide and hydrogen, and it is curious that the E.M.F. should be the same as with air and hydrogen. Siegl states that the current obtainable over a continuous discharge is at the rate of 20 milliamperes per square decimetre of active surface, and that the cost of running in the case of

* *Elektrotechnische Zeitschrift*, Vol. XXXIV., p. 1317, 1912. Abstract in *The Electrician*, Vol. LXXII., p. 609, 1914.

air and coal gas is only 2.04d. per unit. Variation of the gas pressure up to 8 atmospheres did not produce any effect on the E.M.F. The cells were so far commercial that they were taken up by C. Schniewindt, of Neuenrad; but the Author is not aware whether they have been placed on the market.

The principle of the gas cell has been applied by Commelin and Vian to accumulators in which the gas on charging is collected under pressure, but the results do not appear to have been of commercial value.

There seems to be greater difficulty with carbon monoxide than with hydrogen. This is shown to some extent by the

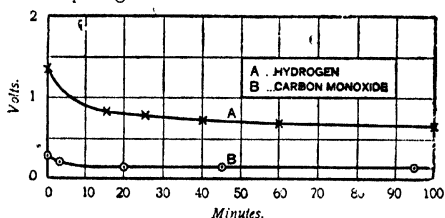


FIG. 204.—Discharge Curves of Gas Cells.

two discharge curves of gas cells given in Fig. 204. The curve A shows the fall of E.M.F. when a small cell containing hydrogen, dilute sulphuric acid and oxygen was connected up to a Weston voltmeter. The substitution of carbon monoxide for hydrogen in this cell gave a very low E.M.F., which, however, increased to 0.3 volt when the sulphuric acid was replaced by a solution of oxalic acid. Curve B shows the discharge of this cell through the same Weston voltmeter. From these curves it appears that the occlusion of carbon monoxide is considerably less rapid than is the case with hydrogen.

Assuming that the conduction takes place by ionised water, the reaction in the case of a hydrogen-oxygen cell may be represented as in Fig. 205, the two plates being regarded as hydrogen and oxygen respectively. It is not

quite so easy, however, to see how the reaction would proceed if carbon monoxide were substituted for hydrogen. The CO might perhaps combine with the OH ion of the water, giving COOH, which is half a molecule of oxalic acid. The same reaction might take place with a solution of oxalic acid in place of water, as indicated in Fig. 206, the CO passing voltaically through the oxalic acid and

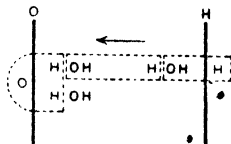


FIG. 205.—Reaction in the Hydrogen-Oxygen Gas Cell.

appearing as the polarising ion at the other plate, to be oxidised by the oxygen. But this reaction is rendered rather improbable by the fact that the molecule of oxalic acid consists of *two* COOH groups, which would have to be separated. Moreover, CO is not an ion of oxalic acid. What is really required for the voltaic oxidation of carbon monoxide is an electrolyte in which CO is one of the ions.

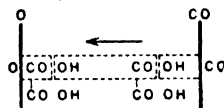


FIG. 206.—Oxalic Acid as the Electrolyte.

BORCHERS' CELL.—A gas cell differing considerably from Grove's was described by W. Borchers in 1894. This inventor appears to have acted on the principle that one of the gases should be absorbed by the electrolyte. He, therefore, selected as an electrolyte a solution of cuprous chloride, either in hydrochloric acid or in ammonium hydrate, on account of its well-known property of absorbing carbon monoxide. The cell consists essentially of a carbon plate in air or oxygen and a copper plate in carbon monoxide, both plates dipping into a solution of cuprous chloride. It is assumed that the carbon monoxide goes into solution

at the copper plate, traverses the electrolyte and is oxidised to carbon dioxide at the carbon plate.

This cell gave very poor results, and it is difficult to see why it should do otherwise. The absorption of carbon monoxide by cuprous chloride is a reaction that takes place under ordinary conditions, and does not require the closing of any circuit; it is therefore unsuitable for voltaic purposes unless the absorption of CO at one plate and its liberation at the other continues upon closing the circuit after the solution is saturated. Moreover, the compound formed by the absorption is an addition product—viz., $\text{Cu}_2\text{Cl}_2\text{CO}$, whereas the ionisation and breaking up of an electrolyte is always necessary in the voltaic formation of a compound.

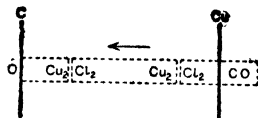


FIG. 207.—Reactions in Borchers' Cell.

Instead of an addition product, we might suppose that the CO is able to combine with one of the ions of the cuprous chloride in some such way as that indicated in Fig. 207. If the Cu_2Cl_2 breaks up, and CO is considered as the electro-positive plate, the Cu will go to the carbon and the chlorine must be looked to for combination with the CO. The compound COCl_2 is known, and its formation would appear probable but for the unfortunate fact that it is a dielectric and at ordinary temperatures it is a gas.

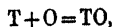
There is no doubt that the E.M.F. observed by Borchers was mainly due to the solution of the copper plate, and not to oxidation of carbon monoxide. This reaction is represented by Fig. 207 if the place of the CO is taken by Cu. The copper migrates across, and is deposited upon the carbon; it does not remain there, however, because the cuprous chloride is oxidised by the oxygen at the carbon

to cupric chloride, and this, in turn, takes up any free copper, re-forming the cuprous salt.

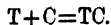
If Borchers' cell depended upon the assumed gas reactions, and were simply a gas cell, the E.M.F. would not be affected by changing the material of the plates, *e.g.*, by having both plates of carbon or of platinum. The capabilities of the cell for supplying current might suffer by such a change, on account of changes in the power of occlusion, but the E.M.F. should remain unaffected. Such, however, is not the case, and we must therefore conclude that the E.M.F. of the cell is not really due to the voltaic oxidation of carbon monoxide.

METHOD OF C. J. REED.—It has been stated by C. J. Reed* that the ideal cell consuming carbon, in any form, should fulfil the following conditions. The cell should consist of two indestructible electrodes immersed in an electrolyte which is held in two compartments separated by a porous partition. This electrolyte, or "transforming substance," should be capable of forming an unstable compound with oxygen and also with carbon, so that in one of the compartments there will be an oxidised body which will readily give up its oxygen, and in the other compartment a carbon compound which may be easily oxidised. When these bodies come together there should be an oxidation of the carbon and regeneration of the transforming substance, so that it does not require renewal.

Reed expresses these changes in the form of equations as follows:—If the transforming substance is represented by T, then by its oxidation we have



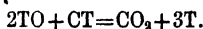
and by its combination with carbon we have



When the compounds TO and TC come into contact by

* *Journal of the Franklin Institute*, Vol. CXLII., p. 1, 1896.

diffusion through the porous pot, they react, giving rise to the E.M.F., and the transforming substance is regenerated according to the equation



The heat evolved by the first two reactions should be as low as possible; but the last reaction, since it gives rise to the E.M.F., should be highly exothermic.

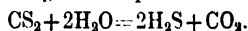
The question of regeneration is no doubt a very important one, for if automatic regeneration is possible, then we may employ a costly electrolyte, which would otherwise render the cell commercially impracticable. It is also important, on account of cheapness, that the plates should be indestructible; but if both plates are to be indestructible, the cell becomes limited to the gas cell type, and the field of investigation is much restricted.

A good deal of difficulty is experienced in attempting to put these principles into practice. But although an ideal transforming substance is not easily found, there are many substances which fulfil the requirements to some extent, and which will indirectly give the required result. Curiously enough none of these appear to be metals.

As an example of how these principles may be applied, Reed takes two transforming substances, viz., sulphur and water, which act together. The fuel is carbon, and atmospheric oxygen is the oxidising agent. The method of working is indicated in Fig. 208

A retort R contains sulphur at I, carbon at F, and a pile of stones at J, on which water is allowed to drop through the tube T'. The retort is heated by burning sulphur at D, the resulting sulphur dioxide passing out of the furnace by the opening S, and being stored for subsequent use. The heating of the retort causes the sulphur at I to be vaporised, and to combine with the red-hot carbon at F to form carbon bisulphide. But when this comes into contact with the steam formed at J, it is decomposed with

the result that sulphuretted hydrogen and carbon dioxide are formed, according to the equation—



As a net result, therefore, of these two sets of reactions we have SO_2 from one, and a mixture of H_2S and CO_2 from the other. These gases are passed through water, giving two solutions, viz., one of sulphurous acid and the other of sulphuretted hydrogen, the small amount of carbon dioxide in the latter being of no importance. Finally, these solutions have to be used so that the sulphur and water are regenerated, and the heat of the reaction is

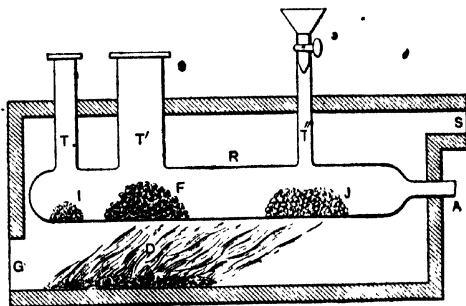
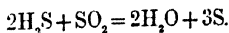


FIG. 203. —Reed's Method

transformed into electrical energy. Reed attempts to do this by separating the solutions by a porous partition and immersing a carbon plate in each. The solutions meet, by diffusing through the porous pot, and react, with the result that the sulphur and water are regenerated according to the following equation:—



It is, however, impossible, that any satisfactory generation of electrical energy should be so effected, for this reaction continues equally on open circuit. The cell is not really a chemical cell, but a liquid cell like that of Becquerel, which accounts for the smallness of the E.M.F.

observed by Reed, viz., 0.36 volt, whereas from the thermo-chemical data the E.M.F. should be 0.63 volt. Even if the higher E.M.F. were obtainable, such a cell would be commercially useless on account of the large amount of local action. These objections apply to Reed's principle as a whole.

UTILISATION OF FREE CARBON.—The cells which we have so far discussed have been attempts to use carbon monoxide. We will now pass to the consideration of cells in which free carbon is used as the active material. One of the greatest difficulties, as already explained, is that of getting the carbon to pass into solution as an ion. According to A. Coehn* this can actually be effected by electrolysing sulphuric acid under certain conditions with an anode of carbon. A deposit, apparently of carbohydrate, is obtained upon a cathode of platinum.

D. Tommasi, many years ago, suggested a cell consisting of carbon opposed to lead peroxide in sulphuric acid: the carbon is the negative pole and it is supposed to be voltaically consumed. But the E.M.F. does not correspond to the thermo-chemical data on that supposition, and the Author finds that if platinum is substituted for carbon the E.M.F. is quite as high though the polarisation is much more rapid. It does not therefore seem clear that the E.M.F. depends essentially upon the carbon; this may assist the depolarisation (regarding oxygen as a polarising ion) either through roughness of surface or through chemical removal of the oxygen, such chemical action not giving rise to any appreciable E.M.F.

W. E. Case states that carbon may be oxidised voltaically by opposing it to platinum in a solution of potassium chlorate rendered acid with sulphuric acid; and he describes a cell in which ferric chloride is reduced by carbon, but the E.M.F. is very small.†

* *Zeitschrift für Elektrochemie*, 1896, pp. 541-542.

† *Electrical World and Engineer*, Vol. XXXIV, p. 121, 1899.

JACQUES' CELL.—The cell which has aroused the greatest interest during the last few years is that which is due to W. W. Jacques.* In this cell, which is illustrated in Fig. 209, the carbon C is immersed in fused caustic soda E; this is contained in an iron vessel I, which also serves as the other plate of the cell. A stream of air is

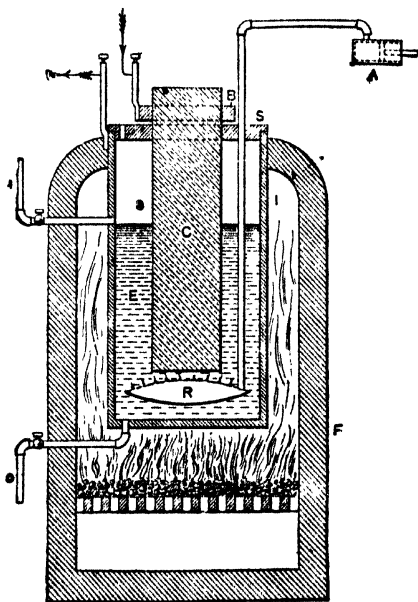


FIG. 209.—Jacques' Cell.

blown through the caustic soda by the pump A, and is distributed by a rose R, which is fixed just below the carbon. The whole cell is kept at a temperature of 400°C. to 500°C. by the furnace F. The stream of air causes the carbon to be oxidised to CO_2 , which is said to mostly bubble

* *The Electrician*, Vol. XXXVI, p. 768, 1896.

up through the electrolyte and to escape. It is stated that the caustic soda is practically unchanged: a certain amount of carbonate, however, does form, and impurities are introduced from the carbon, with the result that the electrolyte ultimately becomes worthless. The formation of carbonate may be diminished by adding a small quantity of magnesia. The E.M.F. of the cell is about 1 volt and the rate of discharge is said to be much higher than that obtainable from other cells of equal weight.

In considering the theory of the cell, it is difficult to see how a truly voltaic oxidation of carbon can take place, at least by means of the oxygen. This gas is forced into the electrolyte in the immediate neighbourhood of the carbon.

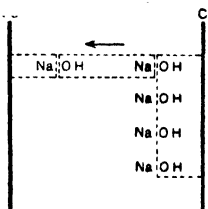


FIG. 210. —Reactions in Jacques' Cell

It is unlikely that the oxygen should assume the function of an ion in the electrolyte, nor is it likely to be occluded by the carbon in a manner similar to that in a gas cell. And even were there such an occlusion, there is no resemblance to a gas battery, in which the oxygen is occluded by the plate that is away from the substance to be oxidised. Here, however, the oxygen is forced directly on to the surface of the carbon, which it is desired to oxidise voltaically, and consequently any oxidation by the oxygen is more likely to be due to ordinary chemical action, or possibly to local action, but not to oxidation of a polarising carbon ion.

Omitting, for a moment, the part played by the oxygen, let us suppose that the carbon is acted upon voltaically by the caustic soda, as indicated in Fig. 210. The carbon is

oxidised to $C(OH)_2$, or carbonic acid, and sodium appears as the polarising ion on the surface of the iron vessel. This reaction, as it stands, is an impossible one, because it is endothermic. The heat of formation of the carbonic acid is less than that of the four molecules of caustic soda, which have to be broken up, and therefore the reaction will not take place. Moreover, iron is electro-positive to carbon, and would be rendered still more so by the polarising sodium. But if the iron is coated with oxide, it may become electro-negative to the carbon, and at the same time it may act as the depolariser, oxidising the sodium. It therefore appears that true voltaic action is unlikely to take place if pure iron is used as one of the plates, but that it might possibly do so if the iron is oxidised, which is an additional reason why the stream of oxygen should be directed on to the iron rather than on to the carbon.

There has been much discussion* as to the origin of the E.M.F. in this cell, and a good deal of evidence has been brought forward in support of the view that the E.M.F. is really thermo-electric, the iron being the hot junction, and the carbon, cooled by the air, being the cold one. For example, according to C. J. Reed, if the carbon is replaced by iron, so that both plates are of the same material, the E.M.F. is increased instead of being diminished. If the stream of air is replaced by one of coal gas the effect is much the same. Further, when the temperature rises on first applying the heat, the carbon is stated to be at first electro-negative to the iron, and then electro-positive. Below the temperature at which the electrolyte has any chemical action on carbon the E.M.F. is considerable, and increases with the temperature to nearly one volt, afterwards diminishing to zero, the carbon then becoming electro-positive; the second maximum does not differ much in value from the maximum electro-negative value.

These facts, however, do not prove definitely that the

* *American Electrician*, Vol. IX., 1897, and Vol. X., 1898.

action is purely thermo-electric. If, for example, the two iron plates in the above experiment are not at the same temperature, which is doubtless the case, the solution of a given quantity of the one plate may evolve more (or less) energy than the deposition of the same quantity at the other plate, with the result that there will be an E.M.F. in the circuit apart from any thermo-electric effect. This is on the assumption that the reactions are the same at the two plates, necessitating an electrolyte with iron ions throughout. The conductivity of the hydroxides of iron at this temperature may, perhaps, be sufficient for this purpose. Or the reactions at the two plates may be different and there may be an E.M.F. due to iron coupled with what is supposed to be iron, but is really an oxide of iron formed by the action of the electrolyte.

It is difficult to separate cause from effect in a case of this kind and to draw a definite conclusion as to whether the E.M.F. is voltaic or thermo-electric. In metallic thermo-electric junctions no chemical change takes place; but in the present case there is electrolysis, which may or may not be a secondary effect. The fact that the Peltier effect between metals and electrolytic solutions is much greater than at purely metallic junctions lends some support to a thermo-electric theory, for the Peltier effect may also be expected to be large between metals and fused electrolytes. Possibly the E.M.F. is both voltaic and thermo-electric.*

The origin of the E.M.F. in a cell of this kind is a question of scientific interest, but from the practical point of view it is of no importance. What is of the highest importance is the cost of running. Unfortunately there are many causes of inefficiency in this cell. In all cells using a fused electrolyte there must be a loss in maintaining the electrolyte in a state of fusion. In this particular cell there must also be a large amount of local action. The carbon dioxide formed is said to escape, but

* F. Haber and L. Bruner (*Electrical Review*, New York, Vol. XLV, p. 514 1904) conclude that the cell is merely a hydrogen-oxygen gas cell.

Edith Thomson states that this is not so when the cell is in action, and that carbonate is formed; thus the life of the electrolyte, which is expensive in first cost, is also short. According to C. J. Reed, the efficiency only amounts to about 8 per cent., and the cost of raw material is at least thirty-four times that for a good steam engine, while the residue or "ash" from the battery would weigh ten or twelve times that from a corresponding steam plant. It is therefore not surprising that the extravagant claims put forward by the inventor have not yet been justified.

BLUMENBERG'S CELL.—This cell, which is illustrated in Fig. 211, closely resembles the Jacques cell. The

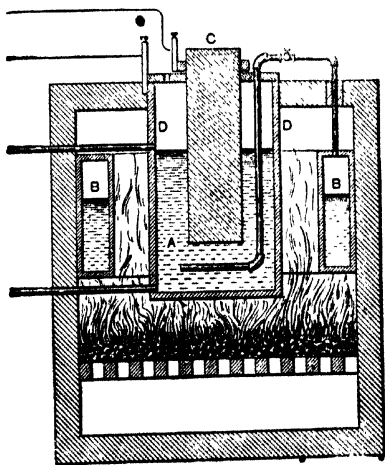


FIG. 211. —Blumenberg's Cell.

carbon C is immersed in an electrolyte of lime, cryolyte and caustic soda A, which is contained in an iron or copper vessel D forming the other plate of the cell. In place of air, a stream of superheated steam, generated in the boiler B, is forced into the electrolyte. The function of the

electrolyte is to oxidise the carbon; its regeneration is effected by the steam which is decomposed. Instead of the electrolyte named, any electrolytic "oxygen bearing" compound may be used.

This cell appears to be open to all the objections urged against the Jacques cell. The only substantial difference between the two is the use of steam in place of air; whether this is an advantage or disadvantage, beyond the elimination of the pump, it is difficult to say; but in any case local action seems to be favoured as far as possible by directing the steam against the carbon. No tests appear to have been made public, and it is unlikely that the problem of the voltaic consumption of carbon is more effectively solved in this cell than it is in that of Jacques.

SHORT'S CELL.—The cell due to H. S. Short is illustrated in Fig. 212. The outer vessel E contains molten

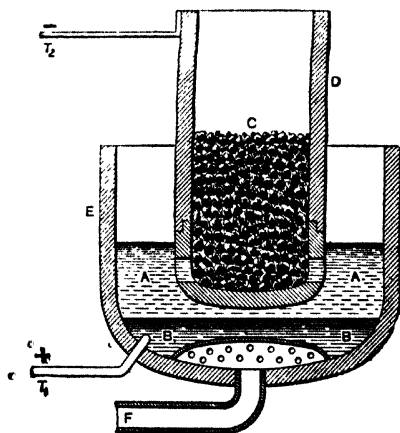


FIG. 212. —Short's Cell.

lead at B above which is fused litharge (PbO), shown at A. Into the litharge there dips an iron vessel D which is

perforated at the bottom and holds the carbon C. The negative terminal T_2 is attached to the vessel D, while the positive terminal T_1 passes into the lead B. We have therefore, what amounts to a plate of carbon opposed to one of lead in an electrolyte of fused litharge. As the carbon is oxidised by the litharge metallic lead is formed as indicated in Fig. 213, and the oxide can be re-formed as desired by blowing air through the tube F.

The voltaic E.M.F. thus appears to be due to the difference in the heats of oxidation of lead and carbon and would in that case approach a zero value (or be slightly negative) if CO_2 were produced, and be negative if CO were the product (i.e., CO could not be produced). The E.M.F. therefore is unlikely to be voltaic, and is

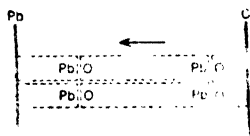


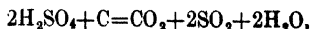
FIG. 213.—Reactions in Short's Cell.

probably thermo-electric. The use of a metal and an oxide in the way suggested is advantageous in that the electrolyte is readily regenerated *in situ*, the lead which is reduced by the action of the cell being re-oxidised by the atmospheric oxygen. This is important, as it reduces both cost of material and cost of handling.

HEATING OF CELLS.—In a cell employing fused electrolytes there must always be some waste of energy in keeping the cell at the required temperature. In order to minimise this loss, W. S. Rawson employs a method of internal combustion which forms the subject of a patent, and is applicable to batteries which generate a current by the action of a fused salt upon a molten metal or alloy,

the salt and metal being separated by a porous partition. The method consists in passing into the metal a mixture of a gas (for example, water gas) and air in such proportions that combustion takes place within the metal, the gas always being maintained slightly in excess, so as to avoid oxidation of the metal. The carbon monoxide and hydrogen of the water gas burn to carbon dioxide and steam, which may be reconverted into water gas by passing through the ordinary generator instead of raising steam for that purpose.

JUNGNER'S CELL.—The cell by E. W. Jungner* is based upon the idea of breaking up sulphuric acid by means of carbon, according to the equation,



the acid being quite strong, or even concentrated, and hot. Coke, or similar amorphous carbon, is used as the electro-

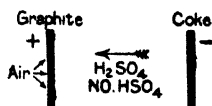


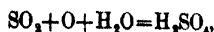
FIG. 214.—Representation of Jungner's Cell.

positive element, and graphite as the electro-negative. The latter is so made that air is forced through it, or against it. Nitrosyl sulphate (presumably the acid sulphate NOHSO_4) is added to the sulphuric acid, and it is stated that when the cell is in action the nitrosyl sulphate is reduced by the coke anode, and is re-oxidised by the stream of air at the cathode. The method is shown as a diagram in Fig. 214.

An extension of the idea seems to be to use the SO_2 so formed in a gas cell containing a porous partition. The

* British patents Nos. 15,727/1906, 5,214/1908 and 5,223/1906. *Centralblatt für Accumulatoren*, Vol. VIII., p. 53, 1907. *Electrochemical Industry*, Vol. VI., p. 259, 1908.

sulphur dioxide is led into one side containing sulphuric acid as the electrolyte, and air or oxygen into the other side containing nitrosyl sulphate in sulphuric acid. The idea is to oxidise the SO_2 into sulphuric acid according to the reaction



thus giving a cyclic process by means of the two cells.

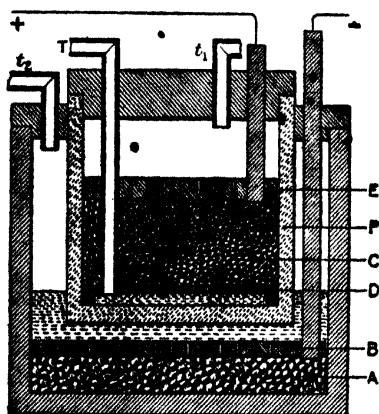


FIG. 215.—Jungner's Cell.

The proposed construction of the carbon cell is shown in Fig. 215. The coke anode is seen at A at the bottom of the containing vessel, and is covered with a perforated graphite plate, B. The graphite cathode C is contained in a porous pot, P, and is kept away from the bottom of this by a perforated plate, D, of ebonite, or some such material. The particles of graphite should not be so small as to draw up the liquid into the spaces by capillarity. The negative pole is a graphite rod fitted into the graphite plate B, and the positive pole is similarly a graphite rod fitted into a graphite

plate, E. Air is forced under the graphite cathode through the tube T, and escapes by the tubes t_1, t_2 . The cell is preferably heated, and is stated to have an E.M.F. varying from 0.5 to 0.3 volt.

Judging by the reactions here described, there is no reason to think that such a cell can be successful. The oxidation of the coke does not take place voltaically. It is an ordinary chemical oxidation, the reduced electrolyte being possibly (if the nitrosyl sulphate is involved) re-oxidised at the cathode. It is more than doubtful if any ions enter into the process. Moreover, concentrated sulphuric acid is, but a poor conductor.

EMISSION OF ELECTRICITY FROM CARBONS AT HIGH TEMPERATURES.—From the theoretical point of view, it is interesting to note that if we have two carbon rods with their ends near together in air, and one of them is heated to a high temperature, a current will flow from the cold rod to the hot one across the gap when their remote ends are metallically connected together. Currents varying from 0.1 to 0.8 ampere were obtained in this way by J. A. Harker and G. W. C. Kaye,* but such a method of obtaining electricity direct from carbon can scarcely give results of practical importance, owing to the difficulty of maintaining high temperatures, except by considerable expenditure of power.

These various attempts to solve the fascinating problem of the direct production of electrical energy from carbon are very interesting from the scientific standpoint; but the results are discouraging, and the difficulties to be overcome appear to be so numerous that there does not seem to be any very great hope that commercial success will be achieved, at least at present.

*Proceedings, Royal Society, Vol. LXXXVI, p. 379, 1912.

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